

Supporting information for

**Visible-Light Induced Cross-Electrophile Coupling of Imines and Anhydrides to
Synthesize α -Amino Ketones**

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Tables of Contents

General methods and materials	S2-S3
Optimization studies	S4-S6
Experimental details and characterization data	S7-S29
Unsuccessful results and up-scaling experiment	S29
Transformations	S29-S31
Experimental details for mechanistic studies	S32-S43
References	S44
Copies of NMR spectra	S45-S87

General methods and materials

Reagents were purchased from commercial suppliers and used as received unless noted otherwise. The Hantzsch ester (HE)^[1] was synthesized according to reported procedures.

Reactions were carried out in dry glassware under a nitrogen atmosphere. For this, the glassware was dried by heat gun under high vacuum (oil pump, 0.1 mbar), cooled to room temperature and backfilled with nitrogen. For the addition of solvents and reagents, syringes and cannula were flushed with nitrogen at least three times before use. All yields are isolated yields, unless otherwise stated. For optimization studies in catalytic reactions, yields were determined from the ¹H-NMR spectrum of the crude product using 1,3,5-trimethoxybenzene as an internal standard, unless noted otherwise. The progress of the reactions was monitored by thin layer chromatography using TLC plates.

Solvents: DMA, DMF, DCM, THF, MeCN and DMSO, were freshly distilled over calcium hydride. Unless otherwise noted, all commercially available reagents were used without further purification. All other reagents were purchased from various commercial sources and used as received.

Thin layer chromatography (TLC) was purchased from commercial suppliers. Compounds were visualized using UV light ($\lambda = 254$ nm) or by applying common staining solution and heating:

KMnO₄ stain: KMnO₄ (3.0 g), Na₂CO₃ (20 g), aq. NaOH solution (5 % w/v, 5.0 mL) in H₂O (300 mL).

Ninhydrin stain: ninhydrin (1.5 g), acetic acid (3.0 mL) in *n*-Butanol (100 mL).

DNP stain: 2,4-dinitrophenylhydrazine (12 g), Conc. H₂SO₄ (60 mL) in EtOH (200 mL) and H₂O (80 mL).

Flash column chromatography was carried out using standard glass columns packed with a plug of cotton wool, silica gel (200-300 mesh) and Na₂SO₄ (1-2 cm).

Melting points (Mp.) were determined on a Mel-TEMP II apparatus and are uncorrected.

Nuclear magnetic resonance (NMR) spectra were measured on a Bruker 400 MHz Fourier transform spectrometers and Bruker 600 MHz Fourier transform spectrometers at East China University of Science and Technology Analytical Testing Centre. ¹H-NMR spectra were measured at 400 or 600 MHz, ¹³C-NMR spectra were measured at 101 or 151 MHz, ¹⁹F-NMR spectra were measured at 377 or 565 MHz. All signals are referenced to the signal of the deuterated solvent (¹H-NMR: CDCl₃, $\delta = 7.26$ ppm; ¹³C-

NMR: CDCl_3 , $\delta = 77.1$ ppm). NMR data are reported as follows: chemical shift (δ/ppm), multiplicity (s: singlet; d: doublet; t: triplet; q: quartett; p: pentett; m: multiplet; brs: broad signal), coupling constants (J/Hz), integration.

High resolution mass spectrometry (HRMS) was performed with a HP1100 LC-MS spectrometer at East China University of Science and Technology Analytical Testing Centre.

Stern-Volmer quenching experiments were performed using a PerkinElmer LS55 Fluorescence Spectrometer.

Reaction Setup A reaction setup containing a 0.6 W, 50 Blue LEDs strip as light source and a case fan as cooling system was used to run the catalysis, see **Figure 1**.

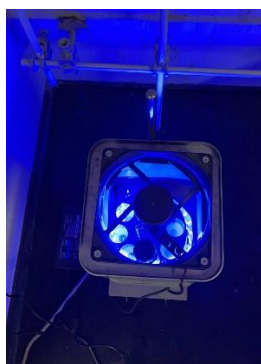
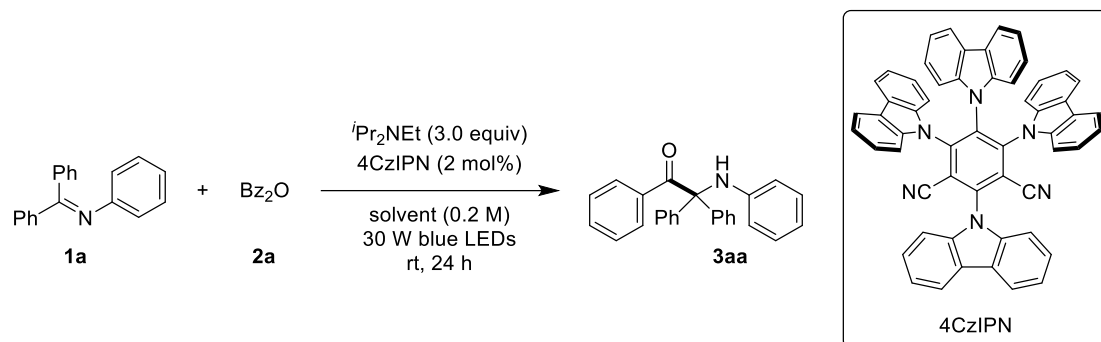


Figure 1. Reaction setup containing blue LED strips and a case fan.

Optimization studies

Table S1: Screening solvents in cross-electrophile coupling reaction

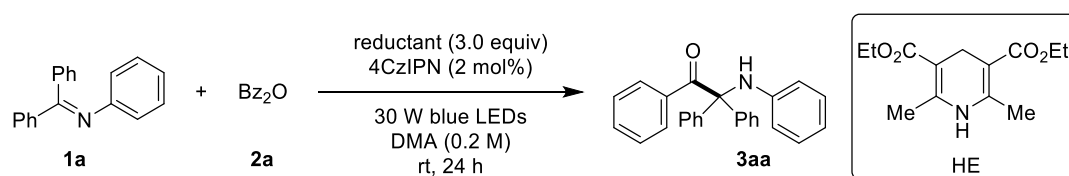


Entry ^a	Solvent	Yield (%) ^b
1	THF	10
2	CH ₂ Cl ₂	30
3	DMSO	25
4	ACN	30
5	DMF	18
6	DMA	32

^a Reaction conditions: **1a** (0.2 mmol), **2a** (2.0 equiv), $i\text{Pr}_2\text{NEt}$ (3.0 equiv) and 4CzIPN (2 mol%) in solvent (1 mL) at rt. The reaction was carried out with blue LEDs in 24 h.

^b Determined by NMR using 1,3,5-trimethoxybenzene as the internal standard.

Table S2: Screening reductant in cross-electrophile coupling reaction

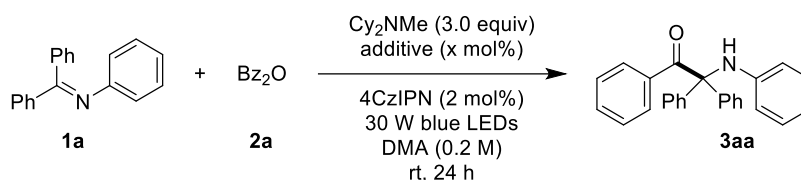


Entry ^a	Reductant	Yield (%) ^b
1	Et ₃ N	41
2	HE	41
3	<i>n</i> -Bu ₃ N	38
4	Cy₂NMe	53

5	<i>i</i> Pr ₂ NEt : Cy ₂ NMe = 1:1	37
6	HE : Cy ₂ NMe = 1:1	34

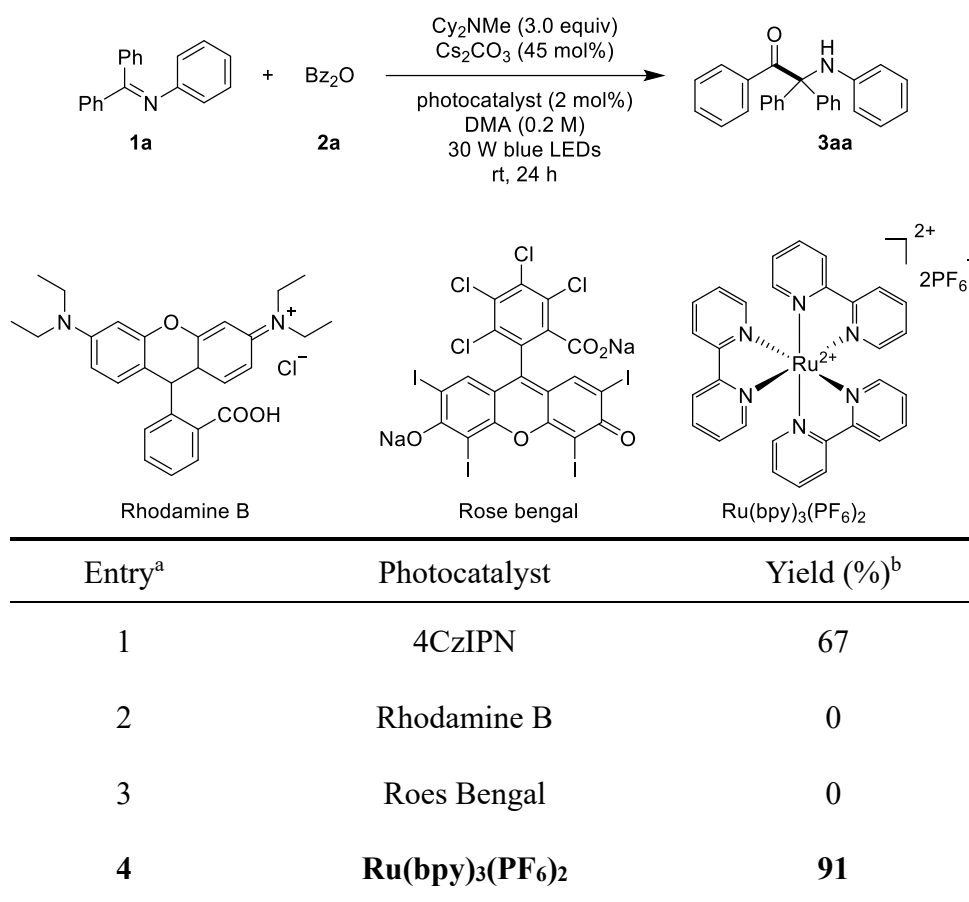
^a Reaction conditions: **1a** (0.2 mmol), **2a** (2.0 equiv), reductant (3.0 equiv) and 4CzIPN (2 mol%) in DMA (1 mL) at rt. The reaction was carried out with blue LEDs in 24 h. ^b Isolated yield.

Table S3: Screening additives in cross-electrophile coupling reaction



Entry ^a	Additive	X	Yield (%) ^b
1	None	0	53
2	BF ₃ ·Et ₂ O	20	30
3	TFA	10	42
4	Li ₂ CO ₃	20	60
5	Cs₂CO₃	45	67(70)^c
6	Cs ₂ CO ₃	100	44
7	K ₃ PO ₄	45	45
8	K ₂ HPO ₄	45	56
9	KH ₂ PO ₄	200	56
10 ^d	Cs ₂ CO ₃	45	32%
11 ^e	Cs ₂ CO ₃	45	50%

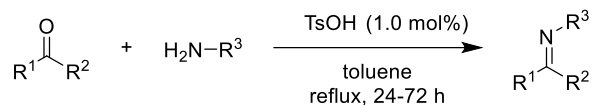
^a Reaction conditions: **1a** (0.2 mmol), **2a** (2.0 equiv), Cy₂NMe (3.0 equiv), additive (x mol%) and 4CzIPN (2 mol%) in DMA (1 mL) at rt. The reaction was carried out with blue LEDs in 24 h. ^b Isolated yield. ^c Reaction time 36 h. ^d DMA (0.5 mL). ^e DMA (2 mL).

Table S4: Screening photocatalysts in cross-electrophile coupling reaction

^a Reaction conditions: **1a** (0.2 mmol), **2a** (2.0 equiv), Cy₂NMe (3.0 equiv), Cs₂CO₃ (45 mol%) and photocatalyst (2 mol%) in DMA (1 mL) at rt. The reaction was carried out with blue LEDs in 24 h. ^b Isolated yield.

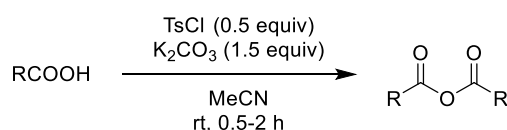
Experimental details and characterization data

General Procedure GP1 - Condensation of ketones and amines



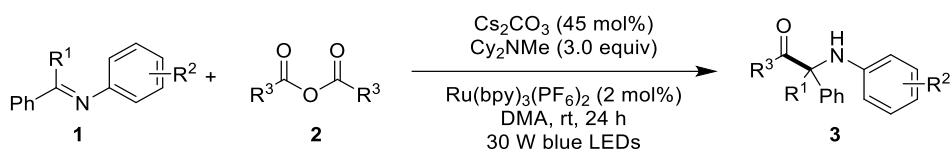
In a modified procedure^[2], ketone (5.0 mmol, 1.0 equiv), amine (5.0 mmol, 1.0 equiv) were dissolved in toluene (10 mL) and then treated with TsOH (8.6 mg, 1 mol%). The resulting mixture was refluxed for 24-72 h. The reaction progress was monitored using TLC. Upon completion of the reaction, the reaction mixture was cooled down to room temperature and then was diluted with EtOAc. The solution was washed with brine (20 mL×1), dried over Na₂SO₄, and concentrated under vacuum. The crude residue was purified by recrystallization or flash chromatography on silica gel using ethyl acetate and petroleum ether as eluents.

General Procedure GP2 – Synthesis of anhydrides



In a modified procedure^[3], carboxylic acid (2.0 mmol, 1.0 equiv), TsCl (141 mg, 0.5 equiv) and K₂CO₃ (414 mg, 1.5 equiv) were dissolved in MeCN (8 mL) and stirred at room temperature for 0.5-2 h. The reaction progress was monitored using TLC. Upon completion of the reaction, the mixture was filtered and washed with CH₂Cl₂, dried over Na₂SO₄, and concentrated under vacuum. The crude material was used for reaction without further purification.

General Procedure GP3 – Photoredox-catalyzed cross-electrophile coupling reaction

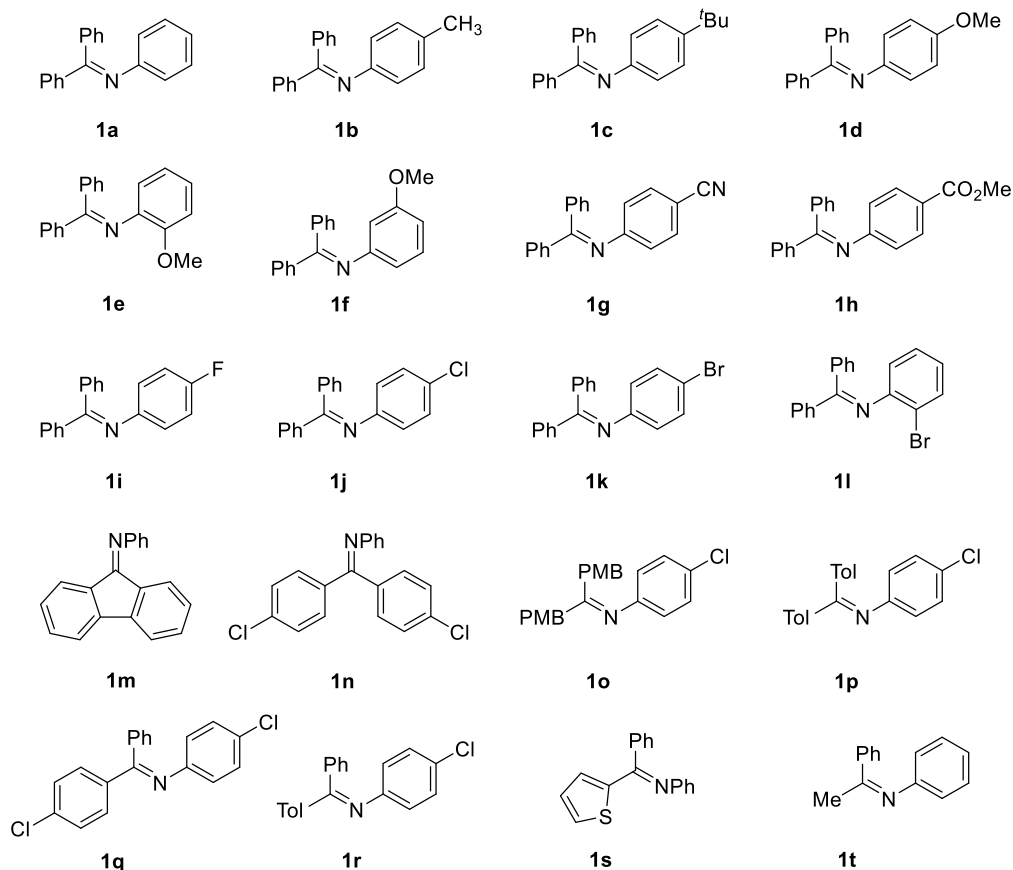


To an oven-dried Schlenk-tube equipped with magnetic stirring was treated with **1** (0.2 mmol), **2** (0.4 mmol, 2.0 equiv), Cs₂CO₃ (29.3 mg, 0.09 mmol, 45 mol%) and Ru(bpy)₃(PF₆)₂ (3.4 mg, 0.004 mmol, 2 mol%). The Schlenk tube was put on vacuum and backfilled with nitrogen three times. Cy₂NMe (128 μL, 0.6 mmol, 3.0 equiv) and DMA (1 mL) were added in the Schlenk tube. The mixture was placed under a 30 W blue LEDs and stirred at ambient temperature. The reaction progress was monitored by TLC. Upon completion of the reaction, ethyl acetate was added to the mixture for extraction. The combined organic layer was dried with anhydrous Na₂SO₄ and

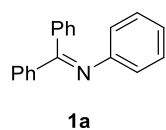
evaporated under vacuum. The residue was purified by silica gel chromatography to provide the desired product **3**.

Reagent and Substrate Synthesis

All ketimines were synthesis according to the general procedure **GP1**.

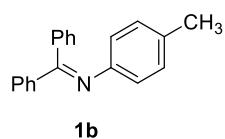


N,1,1-Triphenylmethanimine (**1a**)



Prepared according to the general procedure **GP1**, starting from benzophenone and aniline. The crude residue was purified by recrystallization in ethyl ether. This compound has been reported already. [2]

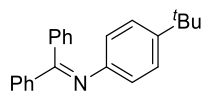
1,1-Diphenyl-N-(p-tolyl)methanimine (**1b**)



Prepared according to the general procedure **GP1**, starting from benzophenone and *p*-toluidine. The crude residue was purified by flash chromatography (eluted with

petroleum ether/EtOAc = 50:1). This compound has been reported already. [2]

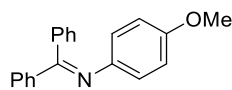
***N*-4-(*tert*-Butyl)phenyl)-1,1-diphenylmethanimine (1c)**



1c

Prepared according to the general procedure **GP1**, starting from benzophenone and 4-(*tert*-butyl)aniline. The crude residue was purified by recrystallization in ethyl ether. This compound has been reported already. [4]

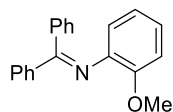
***N*-4-Methoxyphenyl)-1,1-diphenylmethanimine (1d)**



1d

Prepared according to the general procedure **GP1**, starting from benzophenone and 4-methoxyaniline. The crude residue was purified by recrystallization in ethyl ether. This compound has been reported already. [2]

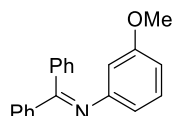
***N*-2-Methoxyphenyl)-1,1-diphenylmethanimine (1e)**



1e

Prepared according to the general procedure **GP1**, starting from benzophenone and 2-methoxyaniline. The crude residue was purified by flash chromatography (eluted with petroleum ether/EtOAc = 50:1). This compound has been reported already. [5]

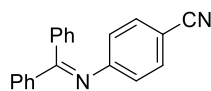
***N*-3-Methoxyphenyl)-1,1-diphenylmethanimine (1f)**



1f

Prepared according to the general procedure **GP1**, starting from benzophenone and 3-methoxyaniline. The crude residue was purified by flash chromatography (eluted with petroleum ether/EtOAc = 30:1). This compound has been reported already. [4]

4-((Diphenylmethylene)amino)benzonitrile (1g)

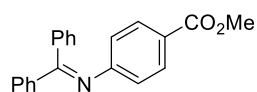


1g

Prepared according to the general procedure **GP1**, starting from benzophenone and 4-

aminobenzonitrile. The crude residue was purified by recrystallization in ethyl ether. This compound has been reported already.^[4]

Methyl 4-((diphenylmethylene)amino)benzoate (1h)

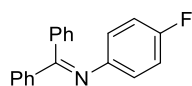


1h

Prepared according to the general procedure **GP1**, starting from benzophenone and methyl 4-aminobenzoate. The crude residue was purified by flash chromatography (eluted with petroleum ether/EtOAc = 50:1).

This compound has been reported already.^[6]

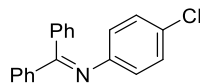
N-(4-Fluorophenyl)-1,1-diphenylmethanimine (1i)



1i

Prepared according to the general procedure **GP1**, starting from benzophenone and 4-fluoroaniline. The crude residue was purified by recrystallization in ethyl ether. This compound has been reported already.^[4]

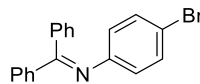
N-(4-Chlorophenyl)-1,1-diphenylmethanimine (1j)



1j

Prepared according to the general procedure **GP1**, starting from benzophenone and 4-chloroaniline. The crude residue was purified by recrystallization in petroleum ether/EtOAc. This compound has been reported already.^[2]

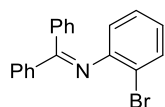
N-(4-Bromophenyl)-1,1-diphenylmethanimine (1k)



1k

Prepared according to the general procedure **GP1**, starting from benzophenone and 4-bromoaniline. The crude residue was purified by recrystallization in ethyl ether. This compound has been reported already.^[4]

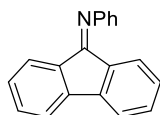
N-(2-Bromophenyl)-1,1-diphenylmethanimine (1l)



1l

Prepared according to the general procedure **GP1**, starting from benzophenone and methyl 4-aminobenzoate. The crude residue was purified by flash chromatography (eluted with petroleum ether). This compound has been reported already.^[7]

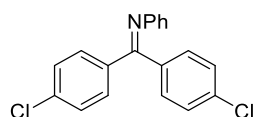
***N*-Phenyl-9H-fluoren-9-imine (1m)**



1m

Prepared according to the general procedure **GP1**, starting from 9H-fluoren-9-one and aniline. The crude residue was purified by recrystallization in ethyl ether. This compound has been reported already.^[8]

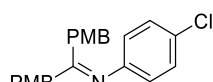
1,1-Bis(4-chlorophenyl)-*N*-phenylmethanimine (1n)



1n

Prepared according to the general procedure **GP1**, starting from bis(4-chlorophenyl)methanone and aniline. The crude residue was purified by recrystallization in EtOH/toluene. This compound has been reported already.^[9]

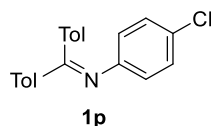
***N*-(4-Chlorophenyl)-1,1-bis(4-methoxyphenyl)methanimine (1o)**



1o

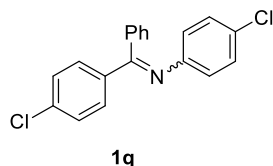
Prepared according to the general procedure **GP1**, starting from bis(4-methoxyphenyl)methanone and 4-chloroaniline. The crude residue was purified by flash chromatography (PE : EA = 30 : 1 as eluent) to give the desired product as a yellow solid in 83% yield. **Mp.** 108-109 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.78 (d, *J* = 8.8 Hz, 2H), 6.65 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 3.79 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 168.0, 161.8, 159.7, 150.3, 132.5, 131.3, 131.2, 128.6, 128.1, 127.9, 122.6, 113.5, 113.4, 55.4, 55.2. **HRMS** (EI, *m/z*): calcd for C₂₁H₁₈ClNO₂: 351.1021, found: 351.1022 [M]⁺.

***N*-(4-Chlorophenyl)-1,1-di-*p*-tolylmethanimine (1p)**



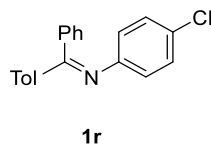
Prepared according to the general procedure **GP1**, starting from di-*p*-tolylmethanone and 4-chloroaniline. The crude residue was purified by recrystallization in ethyl ether to give the desired product as a yellow solid in 41% yield. **Mp.** 118-119 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.16-7.04 (m, 4H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.70-6.60 (m, 2H), 2.41 (s, 3H), 2.33 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 169.0, 150.1, 141.2, 138.7, 137.0, 133.0, 129.5, 129.4, 128.9, 128.7, 128.5, 128.1, 122.4, 21.5, 21.4. **HRMS** (EI, *m/z*): calcd for C₂₁H₁₈ClN: 319.1122, found: 319.1126 [M]⁺.

(E)-N,1-Bis(4-chlorophenyl)-1-phenylmethanimine (1q)



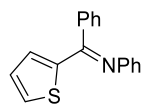
Prepared according to the general procedure **GP1**, starting from (4-chlorophenyl)(phenyl)methanone and 4-chloroaniline. The crude residue was purified by flash chromatography (eluted with petroleum ether/EtOAc = 80:1) to give the desired product as a yellow solid in 29% yield. **Mp.** 90-91 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.78-7.69 (m, 2H), 7.49-7.40 (m, 2H), 7.38-7.28 (m, 3H), 7.21-7.06 (m, 4H), 6.71-6.64 (m, 2H). **¹³C NMR** (101 MHz, CDCl₃) δ 167.7, 149.4, 139.0, 137.8, 137.2, 135.4, 134.9, 134.2, 131.1, 130.8, 130.6, 129.3, 129.0, 128.7, 128.6, 128.5, 128.3, 128.2, 122.3, 122.2. **HRMS** (ESI, *m/z*): calcd for C₁₉H₁₄Cl₂N: 326.0498, found: 326.0502 [M+H]⁺. This mixture exists *E/Z* isomers and the ratio of *E/Z* isomers cannot be identified. However, it does not influence the following reaction.

(E)-N-(4-Chlorophenyl)-1-phenyl-1-(*p*-tolyl)methanimine (1r)



Prepared according to the general procedure **GP1**, starting from phenyl(*p*-tolyl)methanone and 4-chloroaniline. The crude residue was purified by flash chromatography (eluted with petroleum ether/EtOAc = 60:1). This compound has been reported already.^[10]

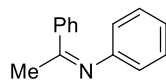
(Z)-N,1-Diphenyl-1-(thiophen-2-yl)methanimine (1s)



1s

Prepared according to the general procedure **GP1**, starting from phenyl(thiophen-2-yl)methanone and aniline. The crude residue was purified by recrystallization in EtOH/toluene. This compound has been reported already.^[2]

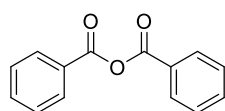
(Z)-N,1-Diphenylethan-1-imine (1t)



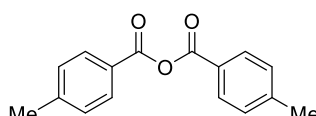
1t

Prepared according to the general procedure **GP1**, starting from acetophenone and aniline. The crude residue was used without further purification. This compound has been reported already.^[8]

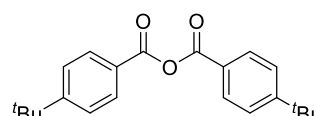
Except for acetic anhydride and benzoic anhydride, which were purchased from commercial suppliers, 2b-2n were synthesized according to GP2.



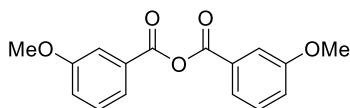
2a



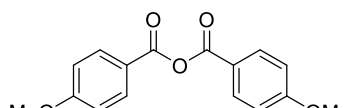
2b



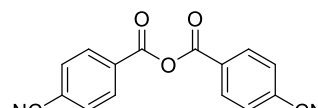
2c



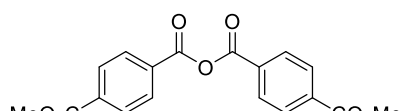
2d



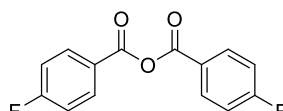
2e



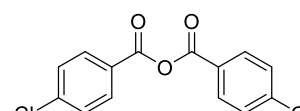
2f



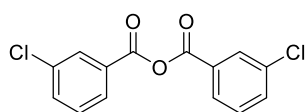
2g



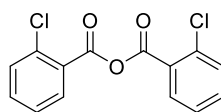
2h



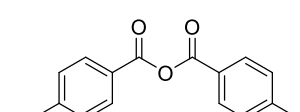
2i



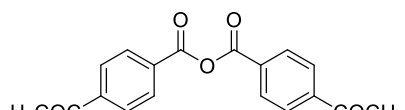
2j



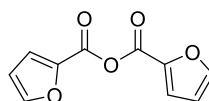
2k



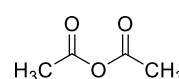
2l



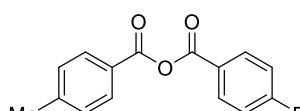
2m



2n

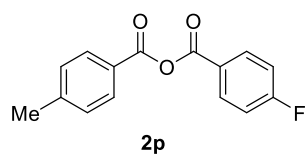


2o



2p

4-Fluorobenzoic 4-methylbenzoic anhydride (2p)

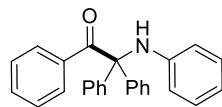


Step 1: 4-methylbenzoic acid (272 mg, 2.0 mmol, 1.0 equiv) was dissolved in DCM (10 mL) and then treated with SOCl_2 (174 μL , 2.4 mmol, 1.2 equiv) and catalytic amount DMF. The resulting mixture was stirred at room temperature for 3 h. Upon completion of the reaction, the mixture was concentrated under vacuum. The crude material was used for reaction without further purification.

Step 2: 4-fluorobenzoic acid (280 mg, 2.0 mmol, 1.0 equiv) was dissolved in toluene (5 mL) and then treated with Et_3N (242 mg, 2.4 mmol, 1.2 equiv) and benzoyl chloride from **Step 1**. The resulting mixture was stirred at room temperature for 12 h. Upon completion of the reaction, ethyl acetate was added to the mixture for extraction. The combined organic layer was dried with anhydrous Na_2SO_4 and evaporated under vacuum. The crude material was confirmed pure by ^1H NMR and directly used for reaction without further purification.

α -Amino ketones

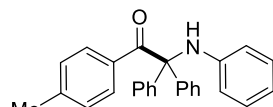
1,2,2-Triphenyl-2-(phenylamino)ethan-1-one (3aa)



3aa

According to **GP3** from **1a** (51.4 mg, 0.2 mmol), **2a** (90.4 mg, 0.4 mmol, 2.0 equiv), Ru(bpy)₃(PF₆)₂ (3.4 mg, 4.0 μ mol, 2 mol%), Cy₂NMe (128 μ L, 0.6 mmol, 3.0 equiv) and Cs₂CO₃ (29.3 mg, 0.09 mmol, 45 mol%) in DMA (1 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 100:1) to give the desired product (66.1 mg, 91% yield) as a yellow solid. **R_f** = 0.60 (petroleum ether/EtOAc = 30:1). **Mp.** 189-190 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.49 (d, *J* = 7.2 Hz, 4H), 7.31-7.13 (m, 9H), 7.06 (t, *J* = 7.6 Hz, 2H), 6.82 (t, *J* = 7.6 Hz, 2H), 6.48 (t, *J* = 7.2 Hz, 1H), 6.28 (d, *J* = 8.0 Hz, 2H), 5.53 (s, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 199.5, 144.7, 140.0, 137.1, 131.8, 129.6, 128.6, 128.6, 128.4, 127.9, 127.6, 117.9, 115.6, 75.2. **HRMS** (ESI, *m/z*): calcd for C₂₆H₂₁NO: 363.1618, found: 363.1595 [M]⁺.

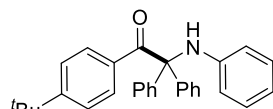
2,2-Diphenyl-2-(phenylamino)-1-(*p*-tolyl)ethan-1-one (3ab)



3ab

According to **GP3** from **1a** (51.4 mg, 0.2 mmol), **2b** (101.6 mg, 0.4 mmol, 2.0 equiv), Ru(bpy)₃(PF₆)₂ (3.4 mg, 4.0 μ mol, 2 mol%), Cy₂NMe (128 μ L, 0.6 mmol, 3.0 equiv) and Cs₂CO₃ (29.3 mg, 0.09 mmol, 45 mol%) in DMA (1 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 50:1) to give the desired product (45.1 mg, 60% yield) as a yellow solid. **R_f** = 0.50 (petroleum ether/EtOAc = 30:1). **Mp.** 160-161 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.67-7.58 (m, 4H), 7.42-7.28 (m, 8H), 7.06-6.93 (m, 4H), 6.67-6.56 (m, 1H), 6.48-6.39 (m, 2H), 5.69 (s, 1H), 2.32 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 198.7, 144.8, 142.7, 140.3, 134.0, 130.1, 128.7 (X 2), 128.6, 128.4, 127.6, 117.9, 115.6, 75.2, 21.6. **HRMS** (EI, *m/z*): calcd for C₂₇H₂₁N: 359.1674, found: 359.1670 [M-H₂O]⁺.

1-(4-(Tert-butyl)phenyl)-2,2-diphenyl-2-(phenylamino)ethan-1-one (3ac)

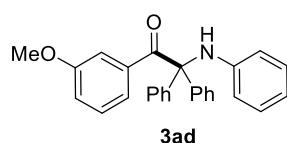


3ac

According to **GP3** from **1a** (51.4 mg, 0.2 mmol), **2c** (135.2 mg, 0.4 mmol, 2.0 equiv), Ru(bpy)₃(PF₆)₂ (3.4 mg, 4.0 μ mol, 2 mol%), Cy₂NMe (128 μ L, 0.6 mmol, 3.0 equiv)

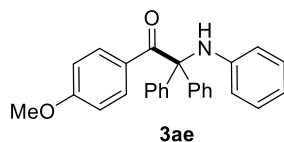
and Cs₂CO₃ (29.3 mg, 0.09 mmol, 45 mol%) in DMA (1 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 50:1) to give the desired product (56.2 mg, 67% yield) as a yellow solid. **R_f** = 0.60 (petroleum ether/EtOAc = 10:1). **Mp.** 218-219 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.65-7.57 (m, 4H), 7.40-7.30 (m, 8H), 7.22 (d, *J* = 8.8 Hz, 2H), 7.06-6.90 (t, *J* = 8.0 Hz, 2H), 6.63-6.57 (t, *J* = 7.2 Hz, 1H), 6.46-6.37 (d, *J* = 7.6 Hz, 2H), 5.71 (s, 1H), 1.28 (s, 9H). **¹³C NMR** (101 MHz, CDCl₃) δ 198.6, 155.4, 144.7, 139.9, 129.8, 128.7, 128.4, 128.3, 127.5, 124.9, 117.7, 115.6, 75.2, 34.9, 31.0. **HRMS** (EI, *m/z*): calcd for C₃₀H₂₇N: 401.2143, found: 401.2151 [M-H₂O]⁺.

1-(3-Methoxyphenyl)-2,2-diphenyl-2-(phenylamino)ethan-1-one (3ad)



According to **GP3** from **1a** (51.4 mg, 0.2 mmol), **2d** (114.0 mg, 0.4 mmol, 2.0 equiv), Ru(bpy)₃(PF₆)₂ (3.4 mg, 4.0 μmol, 2 mol%), Cy₂NMe (128 μL, 0.6 mmol, 3.0 equiv) and Cs₂CO₃ (29.3 mg, 0.09 mmol, 45 mol%) in DMA (1 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/CH₂Cl₂ = 5:1) to give the desired product (50.1 mg, 63% yield) as a yellow solid. **R_f** = 0.60 (petroleum ether/CH₂Cl₂ = 2:1). **Mp.** 152-153 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.63-7.57 (m, 4H), 7.56-7.51 (m, 2H), 7.39-7.24 (m, 6H), 6.97 (m, 2H), 6.73-6.67 (m, 2H), 6.61 (t, *J* = 7.2 Hz, 1H), 6.47-6.39 (d, *J* = 7.6 Hz, 2H), 5.65 (s, 1H), 3.79 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 197.4, 162.5, 144.9, 140.6, 132.5, 128.9, 128.6 (X 2), 128.4, 127.5, 117.8, 115.6, 113.2, 75.1, 55.4. **HRMS** (EI, *m/z*): calcd for C₂₇H₂₁NO: 375.1623, found: 375.1629 [M-H₂O]⁺.

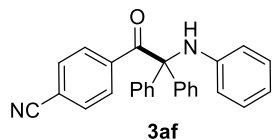
1-(4-Methoxyphenyl)-2,2-diphenyl-2-(phenylamino)ethan-1-one (3ae)



According to **GP3** from **1a** (51.4 mg, 0.2 mmol), **2e** (114.0 mg, 0.4 mmol, 2.0 equiv), Ru(bpy)₃(PF₆)₂ (3.4 mg, 4.0 μmol, 2 mol%), Cy₂NMe (128 μL, 0.6 mmol, 3.0 equiv) and Cs₂CO₃ (29.3 mg, 0.09 mmol, 45 mol%) in DMA (1 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 10:1) to give the desired product (33.4 mg, 42% yield) as a yellow solid. **R_f** = 0.20 (petroleum ether/EtOAc = 10:1). **Mp.** 150-151 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.53-7.45 (m, 4H), 7.44-7.37 (m, 2H), 7.29-7.12 (m, 6H), 6.84 (m, 2H), 6.62-6.54 (m, 2H), 6.48 (t, *J*

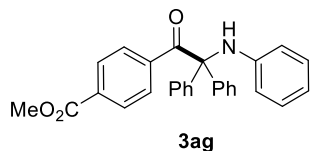
= 7.2 Hz, 1H), 6.35-6.25 (m, 2H), 5.52 (s, 1H), 3.66 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 197.3, 162.5, 144.8, 140.5, 132.4, 128.8, 128.6, 128.5, 128.4, 127.5, 117.8, 115.5, 113.2, 75.0, 55.3. HRMS (ESI, m/z): calcd for $\text{C}_{27}\text{H}_{24}\text{NO}_2$: 394.1802, found: 394.1810 $[\text{M}+\text{H}]^+$.

4-(2,2-Diphenyl-2-(phenylamino)acetyl)benzonitrile (3af)



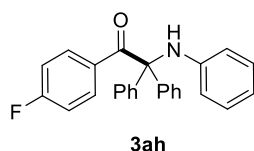
According to **GP3** from **1a** (51.4 mg, 0.2 mmol), **2f** (110.4 mg, 0.4 mmol, 2.0 equiv), $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ (3.4 mg, 4.0 μmol , 2 mol%), Cy_2NMe (128 μL , 0.6 mmol, 3.0 equiv) and Cs_2CO_3 (29.3 mg, 0.09 mmol, 45 mol%) in DMA (1 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 20:1) to give the desired product (41.3 mg, 53% yield) as a yellow solid. R_f = 0.40 (petroleum ether/EtOAc = 10:1). **Mp.** 128-129 $^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ 7.55 (m, 4H), 7.44-7.26 (m, 10H), 6.91 (dd, J = 8.0, 7.2 Hz, 2H), 6.58 (t, J = 7.2 Hz, 1H), 6.32 (d, J = 8.0 Hz, 2H), 5.39 (s, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 199.0, 144.4, 141.3, 139.8, 131.6, 129.6, 128.8, 128.7, 128.1, 128.0, 118.5, 118.0, 115.5, 114.8, 75.1. HRMS (EI, m/z): calcd for $\text{C}_{27}\text{H}_{20}\text{N}_2\text{O}$: 388.1570, found: 388.1582 $[\text{M}]^+$.

Methyl 4-(2,2-diphenyl-2-(phenylamino)acetyl)benzoate (3ag)



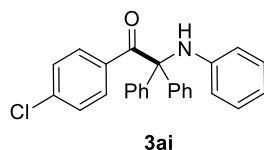
According to **GP3** from **1a** (51.4 mg, 0.2 mmol), **2g** (136.8 mg, 0.4 mmol, 2.0 equiv), $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ (3.4 mg, 4.0 μmol , 2 mol%), Cy_2NMe (128 μL , 0.6 mmol, 3.0 equiv) and Cs_2CO_3 (29.3 mg, 0.09 mmol, 45 mol%) in DMA (1 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 20:1) to give the desired product (57.9 mg, 69% yield) as a yellow solid. R_f = 0.40 (petroleum ether/EtOAc = 10:1). **Mp.** 139-140 $^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, J = 8.4 Hz, 2H), 7.63-7.55 (m, 4H), 7.38-7.30 (m, 8H), 6.94 (m, 2H), 6.64-6.57 (m, 1H), 6.42-6.35 (m, 2H), 5.57 (s, 1H), 3.91 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 199.5, 166.2, 144.5, 141.3, 139.7, 132.4, 129.3, 129.0, 128.7, 128.6, 128.4, 127.8, 118.2, 115.6, 75.2, 52.4. HRMS (ESI, m/z): calcd for $\text{C}_{28}\text{H}_{23}\text{NO}_3\text{Na}$: 444.1570, found: 444.1575 $[\text{M}+\text{Na}]^+$.

1-(4-Fluorophenyl)-2,2-diphenyl-2-(phenylamino)ethan-1-one (3ah)



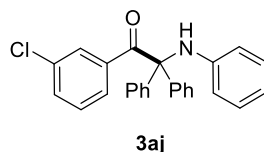
According to **GP3** from **1a** (51.4 mg, 0.2 mmol), **2h** (104.8 mg, 0.4 mmol, 2.0 equiv), Ru(bpy)₃(PF₆)₂ (3.4 mg, 4.0 μmol, 2 mol%), Cy₂NMe (128 μL, 0.6 mmol, 3.0 equiv) and Cs₂CO₃ (29.3 mg, 0.09 mmol, 45 mol%) in DMA (1 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 50:1) to give the desired product (66.0 mg, 86% yield) as a yellow solid. **R_f** = 0.50 (petroleum ether/EtOAc = 30:1). **Mp.** 145-146 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.64-7.55 (m, 4H), 7.49 (m, 2H), 7.44-7.27 (m, 7H), 7.01-6.93 (m, 2H), 6.88 (t, *J* = 8.4 Hz, 2H), 6.62 (t, *J* = 7.2 Hz, 1H), 6.48-6.34 (d, *J* = 8.0 Hz, 2H), 5.54 (s, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 198.0, 165.7 (d, *J*_{C-F} = 254.2 Hz), 144.7, 140.3, 133.1 (d, *J*_{C-F} = 3.3 Hz), 132.4 (d, *J*_{C-F} = 8.9 Hz), 128.7, 128.6, 128.4, 127.7, 118.2, 115.6, 115.1 (d, *J*_{C-F} = 22 Hz), 75.1. **¹⁹F NMR** (377 MHz, CDCl₃) δ -106.40 (m). **HRMS** (EI, *m/z*): calcd for C₂₆H₁₈FN: 363.1423, found: 363.1425 [M-H₂O]⁺.

1-(4-Chlorophenyl)-2,2-diphenyl-2-(phenylamino)ethan-1-one (**3ai**)



According to **GP3** from **1a** (51.4 mg, 0.2 mmol), **2i** (117.6 mg, 0.4 mmol, 2.0 equiv), Ru(bpy)₃(PF₆)₂ (3.4 mg, 4.0 μmol, 2 mol%), Cy₂NMe (128 μL, 0.6 mmol, 3.0 equiv) and Cs₂CO₃ (29.3 mg, 0.09 mmol, 45 mol%) in DMA (1 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 30:1) to give the desired product (53.1 mg, 67% yield) as a yellow solid. **R_f** = 0.40 (petroleum ether/EtOAc = 10:1). **Mp.** 145-146 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.54 (d, *J* = 7.6 Hz, 4H), 7.35-7.24 (m, 9H), 7.17-7.06 (m, 2H), 6.92 (t, *J* = 7.6 Hz, 2H), 6.57 (t, *J* = 7.2 Hz, 1H), 6.35 (d, *J* = 8.0 Hz, 2H), 5.49 (s, 1H). **¹³C NMR** (151 MHz, CDCl₃) δ 198.3, 144.6, 140.1, 138.2, 135.2, 131.1, 128.6, 128.5, 128.3, 128.2, 127.7, 118.2, 115.5, 75.1. **HRMS** (EI, *m/z*): calcd for C₂₆H₁₈NCl: 379.1133, found: 379.1149 [M-H₂O]⁺.

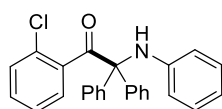
1-(3-Chlorophenyl)-2,2-diphenyl-2-(phenylamino)ethan-1-one (**3aj**)



According to **GP3** from **1a** (51.4 mg, 0.2 mmol), **2j** (117.6 mg, 0.4 mmol, 2.0 equiv), Ru(bpy)₃(PF₆)₂ (3.4 mg, 4.0 μmol, 2 mol%), Cy₂NMe (128 μL, 0.6 mmol, 3.0 equiv)

and Cs₂CO₃ (29.3 mg, 0.09 mmol, 45 mol%) in DMA (1 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 30:1) to give the desired product (57.2 mg, 72% yield) as a yellow solid. **R_f** = 0.40 (petroleum ether/EtOAc = 10:1). **Mp.** 179-180 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.62-7.51 (m, 4H), 7.37-7.21 (m, 8H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.05 (t, *J* = 8.0 Hz, 1H), 6.91 (t, *J* = 8.0 Hz, 2H), 6.57 (t, *J* = 7.2 Hz, 1H), 6.36 (d, *J* = 8.0 Hz, 2H), 5.51 (s, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 198.3, 144.5, 139.8, 138.7, 134.0, 131.7, 129.7, 129.1, 128.7, 128.6, 128.4, 127.8, 127.6, 118.2, 115.6, 75.2. **HRMS** (EI, *m/z*): calcd for C₂₆H₁₈NCl: 379.1133, found: 379.1128 [M-H₂O]⁺.

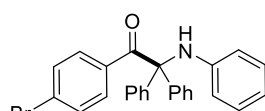
1-(2-Chlorophenyl)-2,2-diphenyl-2-(phenylamino)ethan-1-one (3ak)



3ak

According to **GP3** from **1a** (51.4 mg, 0.2 mmol), **2k** (117.6 mg, 0.4 mmol, 2.0 equiv), Ru(bpy)₃(PF₆)₂ (3.4 mg, 4.0 μmol, 2 mol%), Cy₂NMe (128 μL, 0.6 mmol, 3.0 equiv) and Cs₂CO₃ (29.3 mg, 0.09 mmol, 45 mol%) in DMA (1 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 30:1) to give the desired product (56.2 mg, 71% yield) as a white solid. **R_f** = 0.40 (petroleum ether/EtOAc = 10:1). **Mp.** 139-140 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.51 (m, 4H), 7.30-7.11 (m, 8H), 6.97-6.87 (m, 3H), 6.54 (t, *J* = 7.2 Hz, 1H), 6.41 (d, *J* = 8.0 Hz, 3H), 6.28 (s, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 199.1, 144.0, 137.7, 135.7, 132.9, 130.7, 130.0, 129.6, 128.4, 128.2, 128.1, 127.8, 125.7, 117.6, 116.0, 76.3. **HRMS** (EI, *m/z*): calcd for C₂₆H₂₀ClNO: 397.1228, found: 397.1236 [M]⁺.

1-(4-Bromophenyl)-2,2-diphenyl-2-(phenylamino)ethan-1-one (3al)

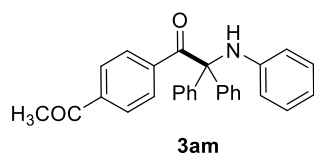


3al

According to **GP3** from **1a** (51.4 mg, 0.2 mmol), **2l** (152.4 mg, 0.4 mmol, 2.0 equiv), Ru(bpy)₃(PF₆)₂ (3.4 mg, 4.0 μmol, 2 mol%), Cy₂NMe (128 μL, 0.6 mmol, 3.0 equiv) and Cs₂CO₃ (29.3 mg, 0.09 mmol, 45 mol%) in DMA (1 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 20:1) to give the desired product (65.0 mg, 74% yield) as a yellow solid. **R_f** = 0.35 (petroleum ether/EtOAc = 10:1). **Mp.** 150-151 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.45 (m, 4H), 7.33-7.12 (m, 10H), 6.90-6.78 (m, 2H), 6.49 (d, *J* = 7.2, 1H), 6.27 (dd, *J* = 7.6, 2.4 Hz, 2H), 5.43 (s, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 198.5, 144.6, 140.0, 135.7, 131.2 (X

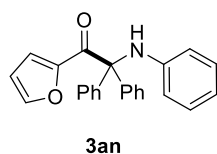
2), 128.7, 128.6, 128.4, 127.8, 126.9, 118.2, 115.5, 75.1. **HRMS** (ESI, m/z): calcd for $C_{26}H_{20}BrNNaO$: 466.0600, found: 466.0638 $[M+Na]^+$.

1-(4-Acetylphenyl)-2,2-diphenyl-2-(phenylamino)ethan-1-one (3am)



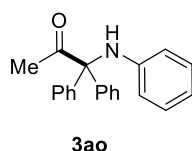
According to **GP3** from **1a** (51.4 mg, 0.2 mmol), **2m** (124.0 mg, 0.4 mmol, 2.0 equiv), $Ru(bpy)_3(PF_6)_2$ (3.4 mg, 4.0 μ mol, 2 mol%), Cy_2NMe (128 μ L, 0.6 mmol, 3.0 equiv) and Cs_2CO_3 (29.3 mg, 0.09 mmol, 45 mol%) in DMA (1 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 20:1) to give the desired product (13.1 mg, 16% yield) as a yellow solid. R_f = 0.30 (petroleum ether/EtOAc = 10:1). **Mp.** 170-171 °C. **1H NMR** (400 MHz, $CDCl_3$) δ 7.73-7.68 (m, 2H), 7.58-7.54 (m, 4H), 7.38-7.26 (m, 8H), 6.95-6.87 (m, 2H), 6.57 (t, J = 7.2 Hz, 1H), 6.39-6.32 (m, 2H), 5.54 (s, 1H), 2.52 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 199.3, 197.4, 144.5, 141.2, 139.7, 138.7, 129.6, 128.7, 128.6, 128.4, 127.7, 118.2, 115.5, 75.1, 26.7. **HRMS** (ESI, m/z): calcd for $C_{28}H_{24}NO_2$: 406.1802, found: 406.1758 $[M+H]^+$

1-(Furan-2-yl)-2,2-diphenyl-2-(phenylamino)ethan-1-one (3an)



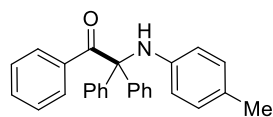
According to **GP3** from **1a** (51.4 mg, 0.2 mmol), **2n** (82.4 mg, 0.4 mmol, 2.0 equiv), $Ru(bpy)_3(PF_6)_2$ (3.4 mg, 4.0 μ mol, 2 mol%), Cy_2NMe (128 μ L, 0.6 mmol, 3.0 equiv) and Cs_2CO_3 (29.3 mg, 0.09 mmol, 45 mol%) in DMA (1 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/ CH_2Cl_2 = 2:1) to give the desired product (40.2 mg, 56% yield) as a yellow solid. R_f = 0.60 (petroleum ether/ CH_2Cl_2 = 1:1). **Mp.** 197-198 °C. **1H NMR** (400 MHz, $CDCl_3$) δ 7.60-7.52 (m, 4H), 7.34-7.21 (m, 7H), 6.95 (m, 2H), 6.82 (dd, J = 3.6, 0.8 Hz, 1H), 6.60 (m, 1H), 6.50-6.41 (m, 2H), 6.29 (dd, J = 3.6, 2.0 Hz, 1H), 5.67 (brs, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 186.8, 151.0, 146.0, 144.8, 140.4, 128.6, 128.3, 128.2, 127.4, 120.5, 118.1, 115.6, 111.9, 73.8. **HRMS** (ESI, m/z): calcd for $C_{24}H_{20}NO_2$: 354.1489, found: 354.1504 $[M+H]^+$.

1,1-Diphenyl-1-(phenylamino)propan-2-one (3ao)



According to **GP3** from **1a** (51.4 mg, 0.2 mmol), **2o** (37.5 μ L, 0.4 mmol, 2.0 equiv), Ru(bpy)₃(PF₆)₂ (3.4 mg, 4.0 μ mol, 2 mol%), Cy₂NMe (128 μ L, 0.6 mmol, 3.0 equiv) and Cs₂CO₃ (29.3 mg, 0.09 mmol, 45 mol%) in DMA (1 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 100:1) to give the desired product (20.0 mg, 33% yield) as a white solid. **R_f** = 0.50 (petroleum ether/EtOAc = 30:1). **Mp.** 165-166 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.61-7.53 (m, 4H), 7.40-7.31 (m, 4H), 7.31-7.22 (m, 2H), 7.01-6.90 (m, 2H), 6.62-6.54 (m, 1H), 6.45-6.36 (m, 2H), 5.78 (s, 1H), 2.14 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 204.8, 144.4, 138.4, 128.8, 128.7, 128.5, 127.8, 117.7, 115.4, 75.3, 26.1. **HRMS** (ESI, m/z): calcd for C₂₁H₂₀NO: 302.1539, found: 302.1542 [M+H]⁺.

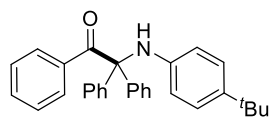
1,2,2-Triphenyl-2-(*p*-tolylamino)ethan-1-one (**3ba**)



3ba

According to **GP3** from **1b** (54.2 mg, 0.2 mmol), **2a** (90.4 mg, 0.4 mmol, 2.0 equiv), Ru(bpy)₃(PF₆)₂ (3.4 mg, 4.0 μ mol, 2 mol%), Cy₂NMe (128 μ L, 0.6 mmol, 3.0 equiv) and Cs₂CO₃ (29.3 mg, 0.09 mmol, 45 mol%) in DMA (1 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 100:1) to give the desired product (60.8 mg, 81% yield) as a yellow solid. **R_f** = 0.60 (petroleum ether/EtOAc = 30:1). **Mp.** 168-169 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.56 (m, 4H), 7.39-7.19 (m, 9H), 7.14 (t, *J* = 7.6 Hz, 2H), 6.71 (d, *J* = 8.0 Hz, 2H), 6.32-6.21 (m, 2H), 5.46 (brs, 1H), 2.09 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 199.6, 142.3, 140.3, 137.1, 131.7, 129.6, 129.1, 128.6, 128.4, 127.9, 127.6, 127.0, 115.6, 75.2, 20.4. **HRMS** (ESI, m/z): calcd for C₂₇H₂₃NNaO: 400.1672, found: 400.1638 [M+Na]⁺.

2-((4-(*tert*-Butyl)phenyl)amino)-1,2,2-triphenylethan-1-one (**3ca**)

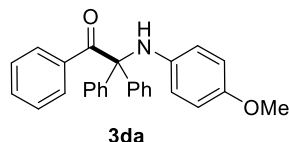


3ca

According to **GP3** from **1c** (62.6 mg, 0.2 mmol), **2a** (90.4 mg, 0.4 mmol, 2.0 equiv), Ru(bpy)₃(PF₆)₂ (3.4 mg, 4.0 μ mol, 2 mol%), Cy₂NMe (128 μ L, 0.6 mmol, 3.0 equiv) and Cs₂CO₃ (29.3 mg, 0.09 mmol, 45 mol%) in DMA (1 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 100:1) to give the desired product (57.1 mg, 68% yield) as a yellow solid. **R_f** = 0.60 (petroleum ether/EtOAc = 30:1). **Mp.** 198-199 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.62-7.54 (m, 4H), 7.35-7.27 (m, 7H), 7.25 (m, 2H), 7.13 (t, *J* = 7.6 Hz, 2H), 6.94-6.87 (m, 2H), 6.35

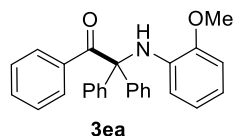
-6.23 (m, 2H), 5.42 (brs, 1H), 1.16 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 199.7, 142.2, 140.6, 140.4, 137.2, 131.6, 129.5, 128.5, 128.4, 127.8, 127.5, 125.3, 115.3, 75.3, 33.7, 31.4. **HRMS** (ESI, m/z): calcd for $\text{C}_{30}\text{H}_{27}\text{N}$: 401.2149, found: 401.2151 $[\text{M}-\text{H}_2\text{O}]^+$.

2-((4-Methoxyphenyl)amino)-1,2,2-triphenylethan-1-one (3da)



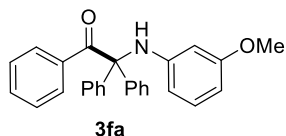
According to **GP3** from **1d** (57.4 mg, 0.2 mmol), **2a** (90.4 mg, 0.4 mmol, 2.0 equiv), $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ (3.4 mg, 4.0 μmol , 2 mol%), Cy_2NMe (128 μL , 0.6 mmol, 3.0 equiv) and Cs_2CO_3 (29.3 mg, 0.09 mmol, 45 mol%) in DMA (1 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 30:1) to give the desired product (50.9 mg, 65% yield) as a white oil. R_f = 0.30 (petroleum ether/EtOAc = 10:1). ^1H NMR (400 MHz, CDCl_3) δ 7.39-7.34 (m, 3H), 7.30-7.25 (m, 10H), 7.19-7.12 (m, 3H), 6.62-6.57 (m, 2H), 6.47-6.42 (m, 2H), 3.62 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 171.1, 158.1, 139.1, 136.8, 134.0, 131.1, 129.6, 129.2, 128.6, 128.1, 127.7, 127.4, 113.4, 64.6, 55.2. **HRMS** (ESI, m/z): calcd for $\text{C}_{27}\text{H}_{24}\text{NO}_2$: 394.1802, found: 394.1810 $[\text{M}+\text{H}]^+$.

2-((2-Methoxyphenyl)amino)-1,2,2-triphenylethan-1-one (3ea)



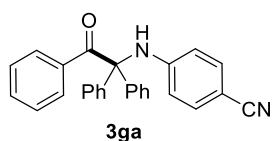
According to **GP3** from **1e** (57.4 mg, 0.2 mmol), **2a** (90.4 mg, 0.4 mmol, 2.0 equiv), $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ (3.4 mg, 4.0 μmol , 2 mol%), Cy_2NMe (128 μL , 0.6 mmol, 3.0 equiv) and Cs_2CO_3 (29.3 mg, 0.09 mmol, 45 mol%) in DMA (1 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 100:1) to give the desired product (62.3 mg, 79% yield) as a yellow solid. R_f = 0.60 (petroleum ether/EtOAc = 30:1). **Mp.** 167-168 $^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ 7.63-7.59 (m, 4H), 7.45-7.40 (m, 2H), 7.36-7.29 (m, 5H), 7.27 (m, 1H), 7.24 (m, 1H), 7.15-7.10 (m, 2H), 6.59 (t, J = 8.0, 1H), 6.51 (m, 2H), 6.17 (dd, J = 7.6, 2.0 Hz, 1H), 6.09 (s, 1H), 3.72 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 199.9, 147.2, 141.4, 136.8, 134.8, 131.5, 129.3, 128.4, 128.0, 127.5, 127.3, 120.4, 117.5, 114.2, 109.3, 74.9, 55.6. **HRMS** (EI, m/z): calcd for $\text{C}_{27}\text{H}_{23}\text{NO}_2$: 393.1723, found: 393.1725 $[\text{M}]^+$.

2-((3-Methoxyphenyl)amino)-1,2,2-triphenylethan-1-one (3fa)



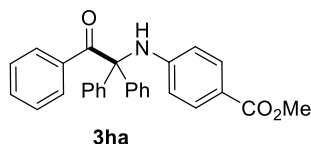
According to **GP3** from **1f** (57.4 mg, 0.2 mmol), **2a** (90.4 mg, 0.4 mmol, 2.0 equiv), Ru(bpy)₃(PF₆)₂ (3.4 mg, 4.0 μmol, 2 mol%), Cy₂NMe (128 μL, 0.6 mmol, 3.0 equiv) and Cs₂CO₃ (29.3 mg, 0.09 mmol, 45 mol%) in DMA (1 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 30:1) to give the desired product (55.2 mg, 70% yield) as a yellow solid. **R_f** = 0.40 (petroleum ether/EtOAc = 10:1). **Mp.** 152-153 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.56 (m, 4H), 7.35-7.22 (m, 9H), 7.20-7.11 (m, 2H), 6.82 (t, *J* = 8.0 Hz, 1H), 6.13 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.00 (dd, *J* = 8.0, 2.0 Hz, 1H), 5.90 (t, *J* = 2.4 Hz, 1H), 5.69 (brs, 1H), 3.53 (s, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ 199.3, 160.0, 146.0, 139.7, 137.0, 131.8, 129.7, 129.3, 128.7, 128.4, 127.9, 127.7, 108.6, 103.6, 101.5, 75.2, 54.9. **HRMS** (EI, *m/z*): calcd for C₂₇H₂₃NO₂: 393.1723, found: 393.1724 [M]⁺.

4-((2-Oxo-1,1,2-triphenylethyl)amino)benzonitrile (**3ga**)



According to **GP3** from **1g** (56.4 mg, 0.2 mmol), **2a** (90.4 mg, 0.4 mmol, 2.0 equiv), Ru(bpy)₃(PF₆)₂ (3.4 mg, 4.0 μmol, 2 mol%), Cy₂NMe (128 μL, 0.6 mmol, 3.0 equiv) and Cs₂CO₃ (29.3 mg, 0.09 mmol, 45 mol%) in DMA (1 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 6:1) to give the desired product (51.4 mg, 66% yield) as a yellow solid. **R_f** = 0.30 (petroleum ether/EtOAc = 5:1). **Mp.** 230-231 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.59-7.49 (m, 4H), 7.45-7.31 (m, 7H), 7.28-7.18 (m, 6H), 6.62 (s, 1H), 6.44 (d, *J* = 8.4 Hz, 2H). **¹³C NMR** (101 MHz, CDCl₃) δ 198.2, 148.1, 137.5, 136.4, 133.1, 132.3, 129.9, 129.0, 128.8, 128.4, 128.2, 120.3, 115.3, 99.7, 75.1. **HRMS** (EI, *m/z*): calcd for C₂₇H₂₀N₂O: 388.1570, found: 388.1581 [M]⁺.

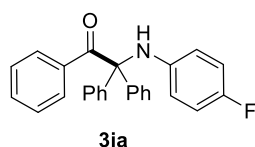
Methyl 4-((2-oxo-1,1,2-triphenylethyl)amino)benzoate (**3ha**)



According to **GP3** from **1h** (63.0 mg, 0.2 mmol), **2a** (90.4 mg, 0.4 mmol, 2.0 equiv), Ru(bpy)₃(PF₆)₂ (3.4 mg, 4.0 μmol, 2 mol%), Cy₂NMe (128 μL, 0.6 mmol, 3.0 equiv) and Cs₂CO₃ (29.3 mg, 0.09 mmol, 45 mol%) in DMA (1 mL). The crude product was

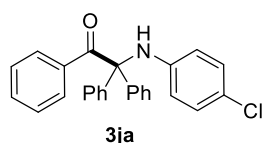
purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 10:1) to give the desired product (62.4 mg, 74% yield) as a yellow solid. R_f = 0.30 (petroleum ether/EtOAc = 10:1). **Mp.** 138-139 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.73-7.62 (m, 2H), 7.57 (m, 4H), 7.43-7.30 (m, 9H), 7.20 (t, J = 8.0 Hz, 2H), 6.43 (m, 3H), 3.81 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 198.6, 167.2, 148.7, 138.4, 136.6, 132.1, 130.8, 129.8, 128.9, 128.6, 128.1, 128.0, 119.1, 114.5, 75.1, 51.5. **HRMS** (EI, m/z): calcd for $\text{C}_{28}\text{H}_{23}\text{NO}_3$: 421.1672, found: 421.1657 [M] $^+$.

2-((4-Fluorophenyl)amino)-1,2,2-triphenylethan-1-one (3ia)



According to **GP3** from **1i** (55.0 mg, 0.2 mmol), **2a** (90.4 mg, 0.4 mmol, 2.0 equiv), $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ (3.4 mg, 4.0 μmol , 2 mol%), Cy_2NMe (128 μL , 0.6 mmol, 3.0 equiv) and Cs_2CO_3 (29.3 mg, 0.09 mmol, 45 mol%) in DMA (1 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 50:1) to give the desired product (55.2 mg, 72% yield) as a yellow solid. R_f = 0.50 (petroleum ether/EtOAc = 30:1). **Mp.** 154-155 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.48 (m, 4H), 7.28-7.15 (m, 9H), 7.07 (m, 2H), 6.53 (s, 2H), 6.26-6.13 (m, 2H), 5.42 (s, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 199.4, 156.0 (d, $J_{\text{C-F}}$ = 237.0 Hz) 141.0 (d, $J_{\text{C-F}}$ = 2.1 Hz), 139.8, 137.0, 134.6, 131.8, 130.6, 129.6, 128.9, 128.6, 128.5, 127.9, 127.7, 116.6 (d, $J_{\text{C-F}}$ = 7.4 Hz), 115.0 (d, $J_{\text{C-F}}$ = 22.3 Hz), 75.5. $^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -127.08 (m). **HRMS** (EI, m/z): calcd for $\text{C}_{26}\text{H}_{20}\text{FNO}$: 381.1523, found: 381.1525 [M] $^+$.

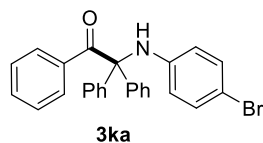
2-((4-Chlorophenyl)amino)-1,2,2-triphenylethan-1-one (3ja)



According to **GP3** from **1j** (58.2 mg, 0.2 mmol), **2a** (90.4 mg, 0.4 mmol, 2.0 equiv), $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ (3.4 mg, 4.0 μmol , 2 mol%), Cy_2NMe (128 μL , 0.6 mmol, 3.0 equiv) and Cs_2CO_3 (29.3 mg, 0.09 mmol, 45 mol%) in DMA (1 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 20:1) to give the desired product (64.3 mg, 81% yield) as a yellow solid. R_f = 0.30 (petroleum ether/EtOAc = 10:1). **Mp.** 118-119 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.53 (d, J = 7.6 Hz, 4H), 7.36-7.25 (m, 9H), 7.15 (t, J = 7.6 Hz, 2H), 6.85 (d, J = 8.4 Hz, 2H), 6.29 (d, J = 8.4 Hz, 2H), 5.76 (s, 1H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 199.0, 143.2, 139.1, 136.8, 131.9, 130.6, 129.6, 128.9, 128.6, 128.5, 128.4, 127.9, 127.8, 122.6, 116.6, 75.2.

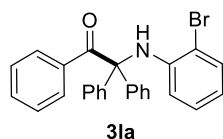
HRMS (ESI, m/z): calcd for $C_{26}H_{20}ClNO_2Na$: 420.1126, found: 420.1144 $[M+Na]^+$.

2-((4-Bromophenyl)amino)-1,2,2-triphenylethan-1-one (3ka)



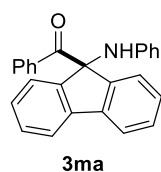
According to **GP3** from **1k** (67.0 mg, 0.2 mmol), **2a** (90.4 mg, 0.4 mmol, 2.0 equiv), $Ru(bpy)_3(PF_6)_2$ (3.4 mg, 4.0 μ mol, 2 mol%), Cy_2NMe (128 μ L, 0.6 mmol, 3.0 equiv) and Cs_2CO_3 (29.3 mg, 0.09 mmol, 45 mol%) in DMA (1 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 20:1) to give the desired product (67.0 mg, 76% yield) as a yellow solid. R_f = 0.30 (petroleum ether/EtOAc = 10:1). **Mp.** 151-152 °C. **1H NMR** (400 MHz, $CDCl_3$) δ 7.55-7.50 (m, 4H), 7.38-7.25 (m, 9H), 7.16 (t, J = 8.0 Hz, 2H), 7.02-6.95 (m, 2H), 6.25 (m, 2H), 5.80 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.0, 143.6, 139.0, 136.8, 131.9, 131.3, 129.7, 128.7, 128.5, 128.0, 127.9, 117.1, 109.8, 75.1. **HRMS** (EI, m/z): calcd for $C_{26}H_{20}BrNO$: 441.0723, found: 441.0723 $[M]^+$.

2-((2-bromophenyl)amino)-1,2,2-triphenylethan-1-one (3la)



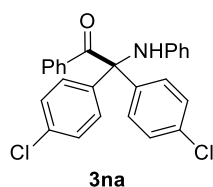
According to **GP3** from **1l** (67.0 mg, 0.2 mmol), **2a** (90.4 mg, 0.4 mmol, 2.0 equiv), $Ru(bpy)_3(PF_6)_2$ (3.4 mg, 4.0 μ mol, 2 mol%), Cy_2NMe (128 μ L, 0.6 mmol, 3.0 equiv) and Cs_2CO_3 (29.3 mg, 0.09 mmol, 45 mol%) in DMA (1 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 100:1) to give the desired product (73.1 mg, 82% yield) as a yellow solid. R_f = 0.60 (petroleum ether/EtOAc = 30:1). **Mp.** 156-157 °C. **1H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.0 Hz, 4H), 7.41 (d, J = 8.4 Hz, 2H), 7.37-7.22 (m, 8H), 7.16 (t, J = 7.6 Hz, 2H), 6.77 (t, J = 7.6 Hz, 1H), 6.47-6.36 (m, 2H), 6.20 (d, J = 8.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.1, 141.7, 140.0, 136.4, 132.1, 131.9, 129.5, 128.5, 128.1, 127.9, 127.7, 127.4, 118.6, 115.3, 111.0, 75.1. **HRMS** (EI, m/z): calcd for $C_{26}H_{18}BrN$: 425.0596, found: 425.0652 $[M-H_2O]^+$.

Phenyl(9-(phenylamino)-9H-fluoren-9-yl)methanone (3ma)



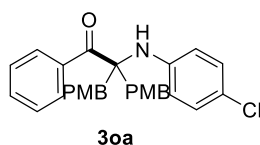
According to **GP3** from **1m** (51.0 mg, 0.2 mmol), **2a** (90.4 mg, 0.4 mmol, 2.0 equiv), Ru(bpy)₃(PF₆)₂ (3.4 mg, 4.0 μmol, 2 mol%), Cy₂NMe (128 μL, 0.6 mmol, 3.0 equiv) and Cs₂CO₃ (29.3 mg, 0.09 mmol, 45 mol%) in DMA (1 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 100:1) to give the desired product (12.2 mg, 17% yield) as a white solid. **R_f** = 0.50 (petroleum ether/EtOAc = 30:1). **Mp.** 178-179 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.86 (d, *J* = 7.6 Hz, 2H), 7.51 (m, *J* = 8.4 Hz, 4H), 7.37 (d, *J* = 7.6 Hz, 3H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 2H), 6.96 (t, *J* = 7.6 Hz, 2H), 6.85 (d, *J* = 7.6 Hz, 2H), 6.61 (t, *J* = 7.2 Hz, 2H), 6.24 (d, *J* = 8.0 Hz, 2H). **¹³C NMR** (101 MHz, CDCl₃) δ 199.2, 144.4, 143.8, 142.1, 136.1, 131.1, 129.6, 128.8, 128.6, 127.7, 127.6, 124.9, 120.8, 117.6, 114.7. **HRMS** (EI, *m/z*): calcd for C₂₆H₁₉NO: 361.1461, found: 361.1471 [M]⁺.

2,2-Bis(4-chlorophenyl)-1-phenyl-2-(phenylamino)ethan-1-one (**3na**)



According to **GP3** from **1n** (65.0 mg, 0.2 mmol), **2a** (90.4 mg, 0.4 mmol, 2.0 equiv), Ru(bpy)₃(PF₆)₂ (3.4 mg, 4.0 μmol, 2 mol%), Cy₂NMe (128 μL, 0.6 mmol, 3.0 equiv) and Cs₂CO₃ (29.3 mg, 0.09 mmol, 45 mol%) in DMA (1 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 80:1) to give the desired product (82.0 mg, 95% yield) as a yellow solid. **R_f** = 0.50 (petroleum ether/EtOAc = 30:1). **Mp.** 135-136 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.50-7.44 (m, 4H), 7.40-7.33 (m, 3H), 7.32-7.27 (m, 4H), 7.20 (t, *J* = 7.6, 2H), 6.98-6.90 (m, 2H), 6.61 (t, *J* = 7.2 Hz, 1H), 6.33 (d, *J* = 7.6 Hz, 2H), 5.50 (s, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 198.8, 144.1, 138.4, 136.4, 133.8, 132.2, 129.9, 129.5, 128.8, 128.8, 128.2, 118.6, 115.7, 74.5. **HRMS** (EI, *m/z*): calcd for C₂₆H₁₇Cl₂N: 413.0738, found: 413.0744 [M-H₂O]⁺.

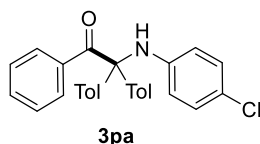
2-((4-Chlorophenyl)amino)-2,2-bis(4-methoxyphenyl)-1-phenylethan-1-one (**3oa**)



According to **GP3** from **1o** (75.8 mg, 0.2 mmol), **2a** (90.4 mg, 0.4 mmol, 2.0 equiv), Ru(bpy)₃(PF₆)₂ (3.4 mg, 4.0 μmol, 2 mol%), Cy₂NMe (128 μL, 0.6 mmol, 3.0 equiv) and Cs₂CO₃ (29.3 mg, 0.09 mmol, 45 mol%) in DMA (1 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 20:1)

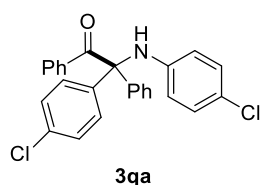
to give the desired product (50.2 mg, 55% yield) as a yellow solid. $R_f = 0.35$ (petroleum ether/EtOAc = 10:1). **Mp.** 154-155 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.44-7.38 (m, 4H), 7.34 (m, 1H), 7.26-7.23 (m, 2H), 7.16 (m, 2H), 6.88-6.80 (m, 6H), 6.33-6.26 (m, 2H), 5.91 (s, 1H), 3.77 (s, 6H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 199.3, 158.9, 143.2, 137.0, 131.7, 130.6, 130.1, 129.6, 128.4, 127.9, 125.5, 122.2, 116.6, 113.8, 74.2, 55.2. **HRMS** (EI, m/z): calcd for $\text{C}_{28}\text{H}_{22}\text{ClNO}_2$: 439.1345, found: 439.1340 $[\text{M}-\text{H}_2\text{O}]^+$.

2-((4-Chlorophenyl)amino)-1-phenyl-2,2-di-*p*-tolylethan-1-one (3pa)



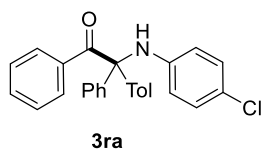
According to **GP3** from **1p** (63.8 mg, 0.2 mmol), **2a** (90.4 mg, 0.4 mmol, 2.0 equiv), $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ (3.4 mg, 4.0 μmol , 2 mol%), Cy_2NMe (128 μL , 0.6 mmol, 3.0 equiv) and Cs_2CO_3 (29.3 mg, 0.09 mmol, 45 mol%) in DMA (1 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 100:1) to give the desired product (71.9 mg, 85% yield) as a yellow solid. $R_f = 0.60$ (petroleum ether/EtOAc = 30:1). **Mp.** 129-130 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.44-7.39 (m, 4H), 7.37-7.30 (m, 3H), 7.17 (t, $J = 8.0$ Hz, 2H), 7.11 (d, $J = 8.4$ Hz, 4H), 6.91-6.82 (m, 2H), 6.35-6.27 (m, 2H), 5.82 (s, 1H), 2.32 (s, 6H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 199.3, 143.4, 137.5, 137.0, 136.1, 131.8, 129.7, 129.2, 128.6, 128.6, 128.4, 127.9, 122.3, 116.6, 74.8, 21.1. **HRMS** (EI, m/z): calcd for $\text{C}_{28}\text{H}_{24}\text{ClNO}$: 425.1541, found: 425.1548 $[\text{M}]^+$.

2-(4-Chlorophenyl)-2-((4-chlorophenyl)amino)-1,2-diphenylethan-1-one (3qa)



According to **GP3** from **1q** (65.0 mg, 0.2 mmol), **2a** (90.4 mg, 0.4 mmol, 2.0 equiv), $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ (3.4 mg, 4.0 μmol , 2 mol%), Cy_2NMe (128 μL , 0.6 mmol, 3.0 equiv) and Cs_2CO_3 (29.3 mg, 0.09 mmol, 45 mol%) in DMA (1 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 40:1) to give the desired product (65.1 mg, 75% yield) as a yellow oil. $R_f = 0.50$ (petroleum ether/EtOAc = 10:1). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.61 (m, 4H), 7.44 (m, 9H), 7.31 (t, $J = 7.6$ Hz, 2H), 6.99 (d, $J = 8.0$ Hz, 2H), 6.40 (d, $J = 8.0$ Hz, 2H), 5.79 (s, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 198.9, 143.1, 139.7, 137.6, 136.7, 133.8, 132.3, 130.5, 129.7, 129.0, 128.7 (X 2), 128.3 (X 2), 128.2, 123.2, 116.8, 75.0. **HRMS** (EI, m/z): calcd for $\text{C}_{26}\text{H}_{19}\text{Cl}_2\text{NO}$: 431.0838, found: 431.0832 $[\text{M}]^+$.

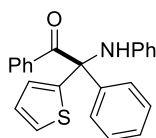
2-((4-Chlorophenyl)amino)-1,2-diphenyl-2-(*p*-tolyl)ethan-1-one (3ra)



3ra

According to **GP3** from **1r** (61.0 mg, 0.2 mmol), **2a** (90.4 mg, 0.4 mmol, 2.0 equiv), Ru(bpy)₃(PF₆)₂ (3.4 mg, 4.0 μmol, 2 mol%), Cy₂NMe (128 μL, 0.6 mmol, 3.0 equiv) and Cs₂CO₃ (29.3 mg, 0.09 mmol, 45 mol%) in DMA (1 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 50:1) to give the desired product (65.3 mg, 79% yield) as a yellow oil. **R_f** = 0.50 (petroleum ether/EtOAc = 30:1). **¹H NMR** (400 MHz, CDCl₃) δ 7.57-7.51 (m, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.32 (m, 6H), 7.15 (m, 4H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.30 (d, *J* = 8.8 Hz, 2H), 5.79 (s, 1H), 2.32 (s, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ 199.2, 143.3, 139.2, 137.6, 136.9, 136.1, 131.9, 129.7, 129.3, 128.7, 128.6, 128.5, 128.4, 127.9, 127.7, 122.5, 116.6, 75.0, 21.1. **HRMS** (EI, *m/z*): calcd for C₂₇H₂₂ClNO: 411.1384, found: 411.1370 [M]⁺.

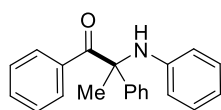
1,2-Diphenyl-2-(phenylamino)-2-(thiophen-2-yl)ethan-1-one (3sa)



3sa

According to **GP3** from **1s** (52.6 mg, 0.2 mmol), **2a** (90.4 mg, 0.4 mmol, 2.0 equiv), Ru(bpy)₃(PF₆)₂ (3.4 mg, 4.0 μmol, 2 mol%), Cy₂NMe (128 μL, 0.6 mmol, 3.0 equiv) and Cs₂CO₃ (29.3 mg, 0.09 mmol, 45 mol%) in DMA (1 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 80:1) to give the desired product (63.2 mg, 85% yield) as a yellow solid. **R_f** = 0.50 (petroleum ether/EtOAc = 30:1). **Mp.** 140-141 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.70-7.61 (m, 2H), 7.35 (t, *J* = 7.6 Hz, 3H), 7.33-7.27 (m, 3H), 7.24 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.17 (t, *J* = 8.0 Hz, 2H), 7.09 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.98-6.89 (m, 3H), 6.60 (t, *J* = 7.6 Hz, 1H), 6.48 (d, *J* = 8.0 Hz, 2H), 6.09 (s, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 198.1, 144.3, 144.2, 139.6, 136.4, 131.9, 129.6, 128.9, 128.5, 128.3, 128.1, 127.9, 127.7, 126.9, 126.4, 118.3, 116.1, 72.9. **HRMS** (EI, *m/z*): calcd for C₂₄H₁₉NOS: 369.1182, found: 369.1183 [M]⁺.

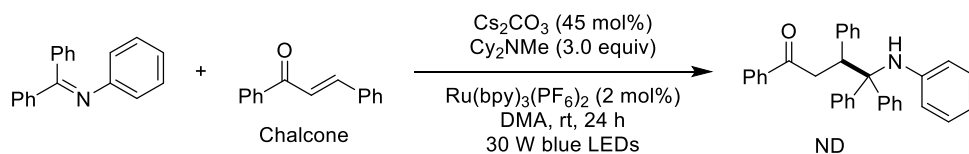
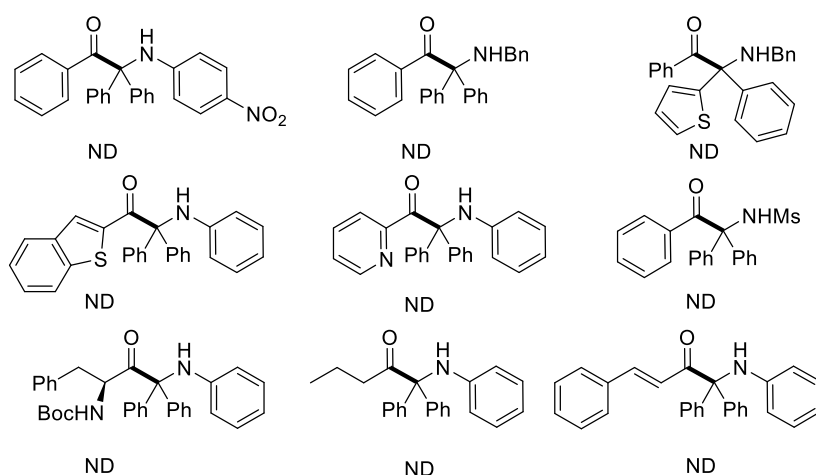
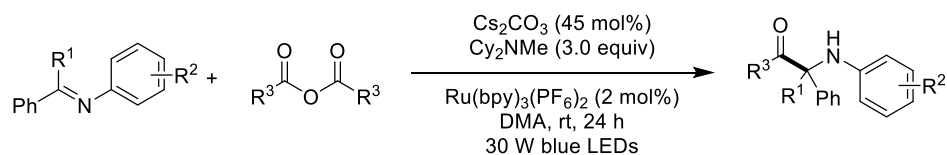
1,2-Diphenyl-2-(phenylamino)propan-1-one (3ta)



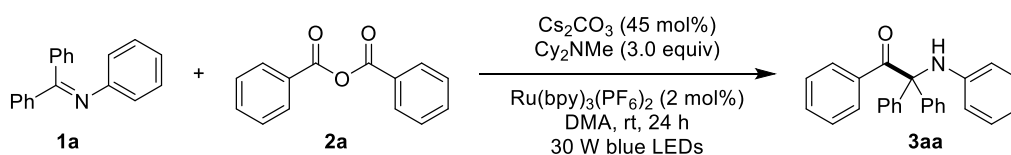
3ta

According to **GP3** from **1t** (39.0 mg, 0.2 mmol), **2a** (90.4 mg, 0.4 mmol, 2.0 equiv), Ru(bpy)₃(PF₆)₂ (3.4 mg, 4.0 μmol, 2 mol%), Cy₂NMe (128 μL, 0.6 mmol, 3.0 equiv) and Cs₂CO₃ (29.3 mg, 0.09 mmol, 45 mol%) in DMA (1 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 50:1) to give the desired product (20.2 mg, 33% yield) as a yellow oil. *R*_f = 0.35 (petroleum ether/EtOAc = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.25 (m, 3H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.05–6.96 (m, 3H), 6.59 (m, 3H), 6.39 (s, 1H), 1.99 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 197.3, 144.7, 144.0, 142.5, 140.4, 135.5, 132.2, 129.8, 128.9, 128.7, 128.4, 128.1, 127.7, 127.5, 127.4, 126.2, 126.2, 117.2, 114.9, 69.5, 17.3. HRMS (EI, *m/z*): calcd for C₂₁H₁₇N: 283.1355, found: 283.1361 [M-H₂O]⁺.

Unsuccessful results



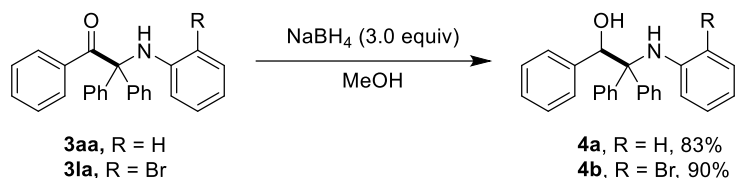
Up-scaling experiment



According to **GP3** from **1a** (1.028 g, 4.0 mmol), **2a** (1.8 g, 8.0 mmol, 2.0 equiv),

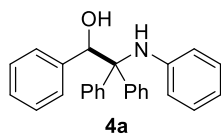
Ru(bpy)₃(PF₆)₂ (68.8 mg, 0.08 mmol, 2 mol%), Cy₂NMe (2.6 mL, 12 mmol, 3.0 equiv) and Cs₂CO₃ (585 mg, 1.8 mmol, 45 mol%) in DMA (20 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 100:1) to give the desired product (1.263 g, 87% yield).

Transformations



3aa (72.6 mg, 0.2 mmol, 1.0 equiv) was dissolved in MeOH (2 mL), and NaBH₄ (22.7 mg, 0.6 mmol, 3.0 equiv) was added to the solution at room temperature. The reaction mixture was stirred for 4 h, and then evaporated under the reduced pressure. The residue was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 10:1) to give the final product **4a** as a white solid (61.2 mg, 83%). **R_f** = 0.25 (petroleum ether/EtOAc = 10:1).

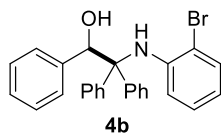
1,2,2-Triphenyl-2-(phenylamino)ethan-1-ol (**4a**)



¹H NMR (400 MHz, CDCl₃) δ 7.68-7.59 (m, 2H), 7.35 (d, *J* = 6.8 Hz, 5H), 7.22 (m, 4H), 7.15 (t, *J* = 7.6 Hz, 2H), 6.92 (t, *J* = 7.6 Hz, 2H), 6.86 (d, *J* = 7.6 Hz, 2H), 6.57 (t, *J* = 7.2 Hz, 1H), 6.30 (d, *J* = 8.0 Hz, 2H), 5.50 (d, *J* = 4.4 Hz, 1H), 5.13 (s, 1H), 2.26 (d, *J* = 4.4 Hz, 1H). This compound has been reported already.^[11]

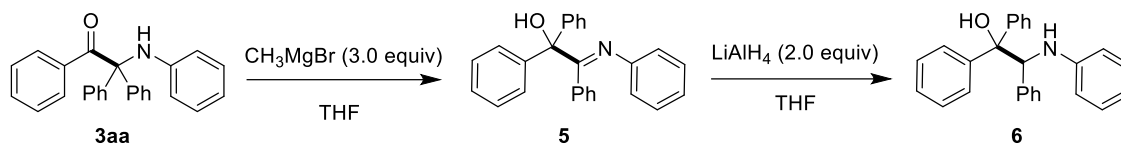
3la (132.3 mg, 0.3 mmol, 1.0 equiv) was dissolved in MeOH (3 mL), and NaBH₄ (34 mg, 0.9 mmol, 3.0 equiv) was added to the solution at room temperature. The reaction mixture was stirred for 4 h, and then evaporated under the reduced pressure. The residue was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 20:1) to give the final product **4b** as a colorless oil (120 mg, 90%). **R_f** = 0.20 (petroleum ether/EtOAc = 30:1).

2-((2-Bromophenyl)amino)-1,2,2-triphenylethan-1-ol (**4b**)



¹H NMR (400 MHz, CDCl₃) δ 7.73-7.59 (m, 2H), 7.49-7.38 (m, 6H), 7.29 (dd, *J* = 6.0, 2.8 Hz, 4H), 7.21 (t, *J* = 7.6 Hz, 2H), 6.99 (d, *J* = 7.2 Hz, 2H), 6.74-6.64 (m, 1H), 6.46

(t, $J = 7.6$ Hz, 1H), 6.00 (d, $J = 8.4$ Hz, 1H), 5.90 (s, 1H), 5.56 (d, $J = 3.6$ Hz, 1H), 2.32 (d, $J = 4.0$ Hz, 1H). This compound has been reported already.^[11]



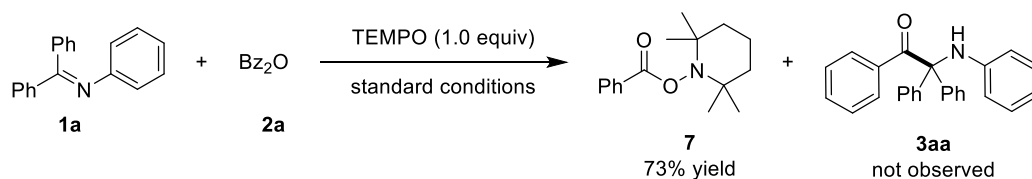
(*E*)-1,1,2-Triphenyl-2-(phenylimino)ethan-1-ol (5): To an oven-dried Schlenk-tube equipped with magnetic stirring was treated with **3aa** (109 mg, 0.3 mmol, 1.0 equiv). The Schlenk tube was put on vacuum and backfilled with nitrogen three times. THF (3 mL) were added in the Schlenk tube and the mixture was cooled to 0 °C. CH₃MgBr (0.9 mL, 0.9 mmol, 3.0 equiv) was added dropwise. After that, the solution was heated to reflux for 4 h. Upon completion of the reaction, the reaction mixture was quenched by H₂O and extracted with ethyl acetate. The combined organic layer was dried with anhydrous Na₂SO₄ and evaporated under vacuum. The residue was purified by silica gel chromatography (eluted with petroleum ether/EtOAc = 100:1 to 20:1) to provide the desired product **5** as colorless oil (105 mg, 96%). **R_f** = 0.30 (petroleum ether/EtOAc = 30:1). **¹H NMR** (400 MHz, CDCl₃) δ 7.48-7.43 (m, 4H), 7.34-7.29 (m, 6H), 7.17-7.08 (m, 3H), 7.00-6.93 (m, 3H), 6.85 (brs, 1H), 6.75 (d, $J = 8.0$ Hz, 2H), 6.51 (d, $J = 8.0$ Hz, 2H). **¹³C NMR** (101 MHz, CDCl₃) δ 173.9, 147.9, 142.0, 134.8, 129.3, 128.7, 128.5, 127.8, 127.7, 127.5, 124.3, 121.3, 82.2. **HRMS** (EI, m/z): calcd for C₂₆H₂₁NO: 363.1618, found: 363.1621 [M]⁺.

1,1,2-Triphenyl-2-(phenylamino)ethan-1-ol (6)

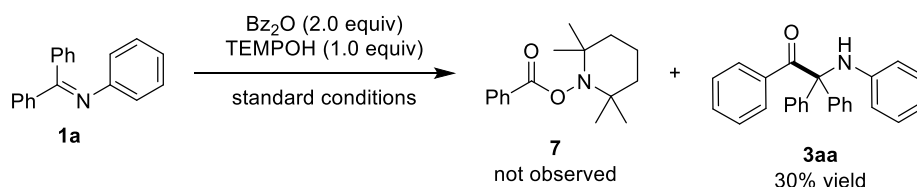
5 (105 mg, 0.289 mmol, 1.0 equiv) was dissolved in THF (4 mL), and LiAlH₄ (21.9 mg, 0.578 mmol, 2.0 equiv) was added to the solution at room temperature. The reaction mixture was stirred for 10 min. Upon completion of the reaction, the reaction mixture was quenched by H₂O and extracted with ethyl acetate. The combined organic layer was dried with anhydrous Na₂SO₄ and evaporated under vacuum. The residue was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 25:1) to give the desired product **6** as yellow solid (93.1 mg, 88%). **R_f** = 0.20 (petroleum ether/EtOAc = 10:1). **¹H NMR** (400 MHz, CDCl₃) δ 7.55 (dd, $J = 7.2, 1.6$ Hz, 2H), 7.37-7.32 (m, 2H), 7.28 (dd, $J = 6.8, 2.0$ Hz, 1H), 7.20-6.97 (m, 12H), 6.65 (t, $J = 7.2$ Hz, 1H), 6.46 (d, $J = 8.4$ Hz, 2H), 5.32 (s, 1H), 4.68 (brs, 1H), 2.78 (s, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 146.6, 144.8, 143.9, 138.0, 129.1, 128.7, 128.4, 128.0, 127.9, 127.5, 127.4, 126.9 (x 2), 125.9, 117.4, 113.4, 81.2, 64.1. This compound has been reported already.^[12]

Mechanistic studies

TEMPO radical-trapping experiment

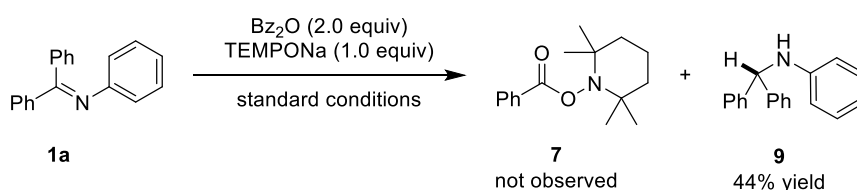


To an oven-dried Schlenk-tube equipped with magnetic stirring was treated with **1a** (51.4 mg, 0.2 mmol, 1.0 equiv), **2a** (90.4 mg, 0.4 mmol, 2.0 equiv), Cs₂CO₃ (29.3 mg, 0.09 mmol, 45 mol%), Ru(bpy)₃(PF₆)₂ (3.4 mg, 0.004 mmol, 2 mol%) and TEMPO (31.3 mg, 0.2 mmol, 1.0 equiv). The Schlenk tube was put on vacuum and backfilled with nitrogen three times. Cy₂NMe (128 μL, 0.6 mmol, 3.0 equiv) and DMA (1 mL) were added in the Schlenk tube. The mixture was placed under a 30 W blue LEDs and stirred at ambient temperature. The reaction progress was monitored by TLC. Upon completion of the reaction, ethyl acetate was added to the mixture for extraction. The combined organic layer was dried with anhydrous Na₂SO₄ and evaporated under vacuum. The residue was purified by silica gel chromatography (eluted with petroleum ether/EtOAc = 100:1) to provide the desired product **7** as a yellow solid (36.1 mg, 73%). **R_f** = 0.40 (petroleum ether/EtOAc = 30:1). ¹H NMR (400 MHz, CDCl₃) δ 8.21-8.00 (m, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 1.84-1.64 (m, 3H), 1.62-1.53 (m, 2H), 1.44 (m, 1H), 1.27 (s, 6H), 1.11 (s, 6H). This compound has been reported already.^[13]



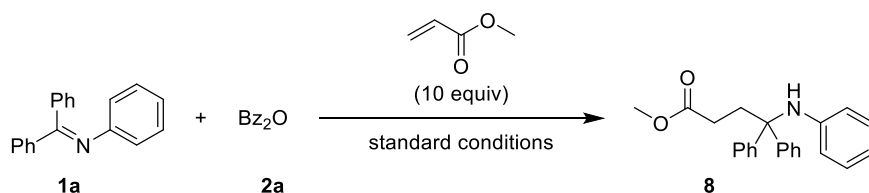
To an oven-dried Schlenk-tube equipped with magnetic stirring was treated with **1a** (51.4 mg, 0.2 mmol, 1.0 equiv), **2a** (90.4 mg, 0.4 mmol, 2.0 equiv), Cs₂CO₃ (29.3 mg, 0.09 mmol, 45 mol%), Ru(bpy)₃(PF₆)₂ (3.4 mg, 0.004 mmol, 2 mol%) and TEMPOH (31.5 mg, 0.2 mmol, 1.0 equiv). The Schlenk tube was put on vacuum and backfilled with nitrogen three times. Cy₂NMe (128 μL, 0.6 mmol, 3.0 equiv) and DMA (1 mL) were added in the Schlenk tube. The mixture was placed under a 30 W blue LEDs and stirred at ambient temperature. The reaction progress was monitored by TLC. Upon completion of the reaction, ethyl acetate was added to the mixture for extraction. The combined organic layer was dried with anhydrous Na₂SO₄ and evaporated under vacuum. The residue was purified by silica gel chromatography (eluted with petroleum

ether/EtOAc = 100:1) to provide product **3aa** as a yellow solid (22.1 mg, 30%).



To an oven-dried Schlenk-tube equipped with magnetic stirring was treated with **1a** (51.4 mg, 0.2 mmol, 1.0 equiv), **2a** (90.4 mg, 0.4 mmol, 2.0 equiv), Cs₂CO₃ (29.3 mg, 0.09 mmol, 45 mol%), Ru(bpy)₃(PF₆)₂ (3.4 mg, 0.004 mmol, 2 mol%) and TEMPONa (35.8 mg, 0.2 mmol, 1.0 equiv). The Schlenk tube was put on vacuum and backfilled with nitrogen three times. Cy₂NMe (128 μL, 0.6 mmol, 3.0 equiv) and DMA (1 mL) were added in the Schlenk tube. The mixture was placed under a 30 W blue LEDs and stirred at ambient temperature. The reaction progress was monitored by TLC. Upon completion of the reaction, ethyl acetate was added to the mixture for extraction. The combined organic layer was dried with anhydrous Na₂SO₄ and evaporated under vacuum. The residue was purified by silica gel chromatography (eluted with petroleum ether/EtOAc = 100:1) to provide product **9** as a white oil (23.1 mg, 44%). ¹H NMR (400 MHz, CDCl₃) δ 7.31-7.13 (m, 10H), 7.07-6.99 (m, 2H), 6.61 (t, *J* = 7.2 Hz, 1H), 6.46 (d, *J* = 8.0 Hz, 2H), 5.41 (s, 1H), 4.14 (brs, 1H). This compound has been reported already.^[11]

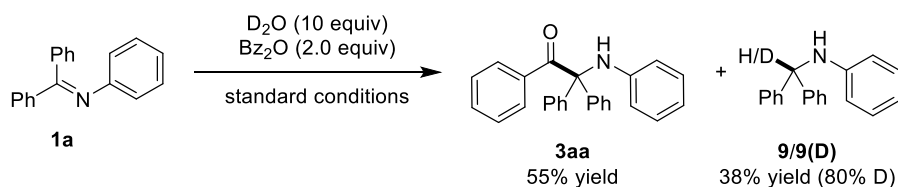
Methyl acrylate radical-trapping experiment



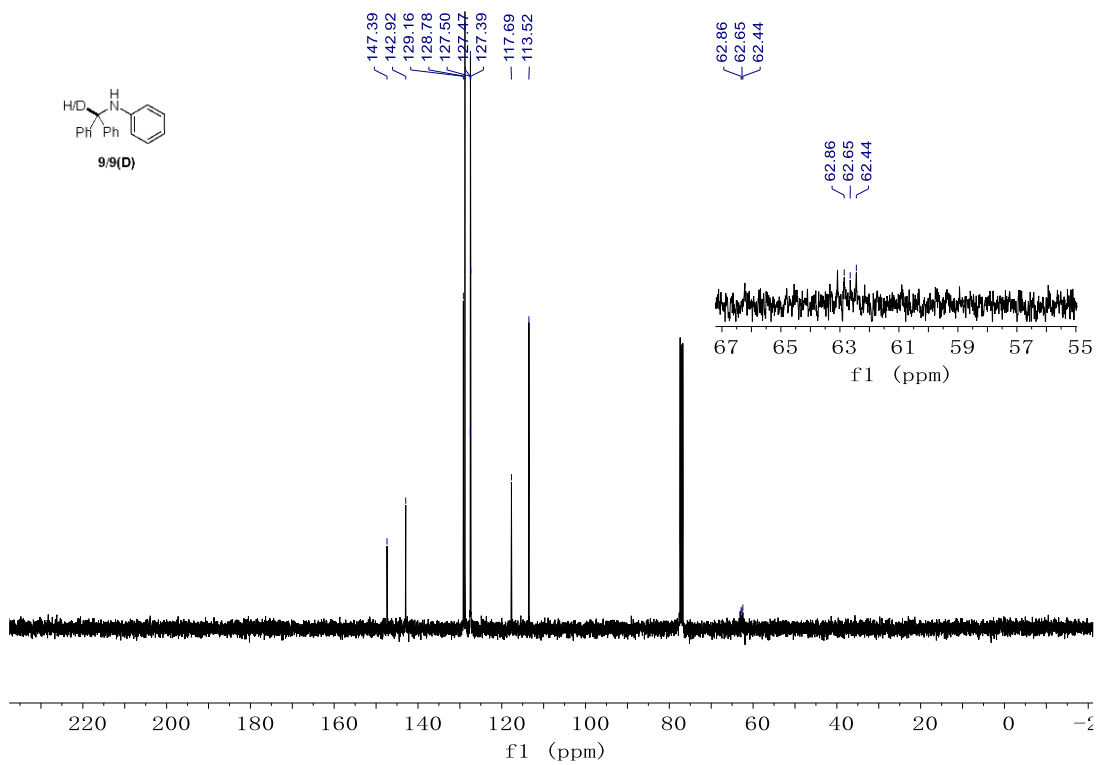
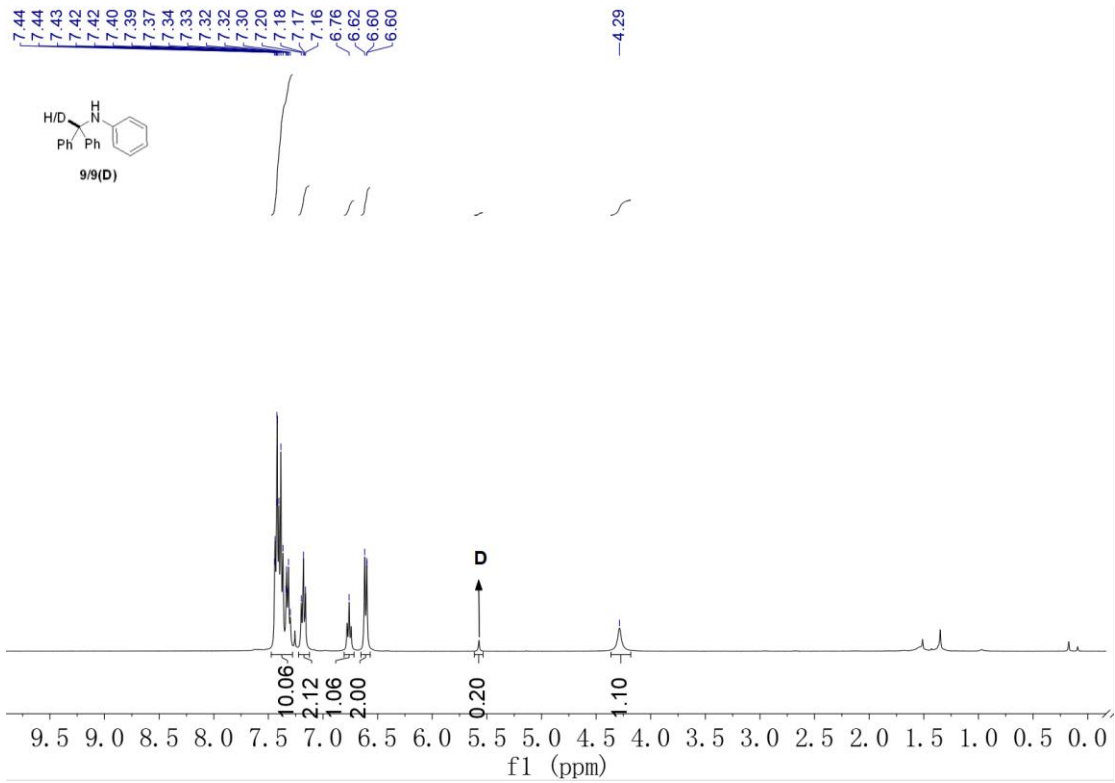
To an oven-dried Schlenk-tube equipped with magnetic stirring was treated with **1a** (51.4 mg, 0.2 mmol, 1.0 equiv), **2a** (90.4 mg, 0.4 mmol, 2.0 equiv), Cs₂CO₃ (29.3 mg, 0.09 mmol, 45 mol%), Ru(bpy)₃(PF₆)₂ (3.4 mg, 0.004 mmol, 2 mol%) and methyl acrylate (180 μL, 2.0 mmol, 10 equiv). The Schlenk tube was put on vacuum and backfilled with nitrogen three times. Cy₂NMe (128 μL, 0.6 mmol, 3.0 equiv) and DMA (1 mL) were added in the Schlenk tube. The mixture was placed under a 30 W blue LED and stirred at ambient temperature. The reaction progress was monitored by TLC. Upon completion of the reaction, ethyl acetate was added to the mixture for extraction. The combined organic layer was dried with anhydrous Na₂SO₄ and evaporated under vacuum. The residue was purified by silica gel chromatography (eluted with petroleum

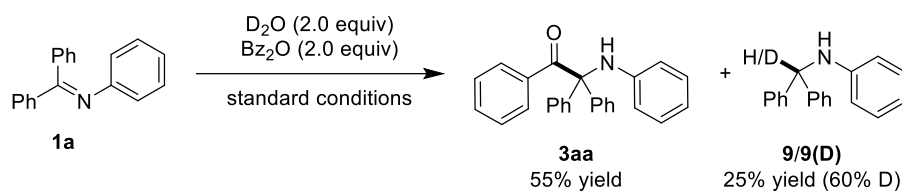
ether/EtOAc = 30:1) to provide the desired product **8** as a yellow oil (40.0 mg, 58%). $R_f = 0.25$ (petroleum ether/EtOAc = 30:1). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.60-7.54 (m, 4H), 7.36 (t, $J = 7.6$ Hz, 4H), 7.29-7.22 (m, 2H), 7.09-7.01 (m, 2H), 6.70 (t, $J = 7.6$ Hz, 1H), 6.48 (d, $J = 7.6$ Hz, 2H), 4.72 (s, 1H), 3.62 (s, 3H), 3.03 -2.93 (m, 2H), 2.30 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 174.1, 145.4, 145.2, 128.8, 128.6, 126.9, 126.8, 118.1, 116.2, 64.7, 51.7, 32.5, 29.3. **HRMS** (EI, m/z): calcd for $\text{C}_{23}\text{H}_{23}\text{NO}_2$: 345.1723, found: 345.1725 $[\text{M}]^+$.

Deuterium-labeling experiment

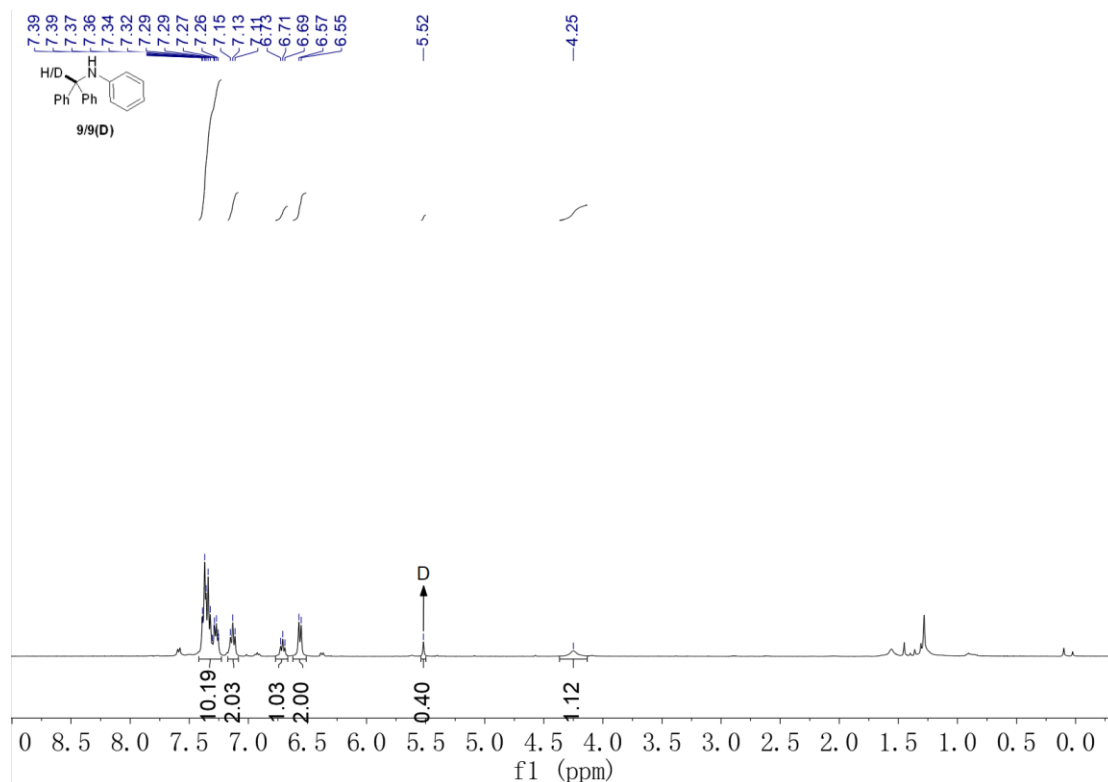


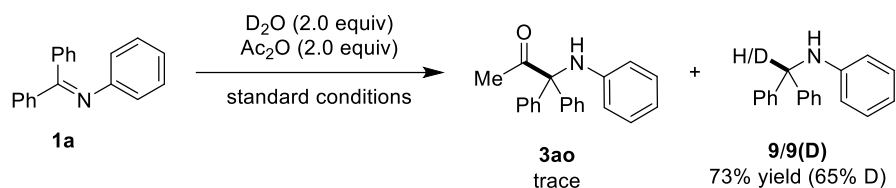
To an oven-dried Schlenk-tube equipped with magnetic stirring was treated with **1a** (51.4 mg, 0.2 mmol, 1.0 equiv), **2a** (90.4 mg, 0.4 mmol, 2.0 equiv), Cs_2CO_3 (29.3 mg, 0.09 mmol, 45 mol%), $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ (3.4 mg, 0.004 mmol, 2 mol%) and D_2O (36 μL , 2.0 mmol, 10 equiv). The Schlenk tube was put on vacuum and backfilled with nitrogen three times. Cy_2NMe (128 μL , 0.6 mmol, 3.0 equiv) and DMA (1 mL) were added in the Schlenk tube. The mixture was placed under a 30 W blue LED and stirred at ambient temperature. The reaction progress was monitored by TLC. Upon completion of the reaction, ethyl acetate was added to the mixture for extraction. The combined organic layer was dried with anhydrous Na_2SO_4 and evaporated under vacuum. The residue was purified by silica gel chromatography (eluted with petroleum ether/EtOAc = 30:1) to provide the product **3aa** (40.0 mg, 55%) and **9/9(D)** (20.1 mg, 38%, 80% D) as a white oil. **HRMS** (EI, m/z): calcd for $\text{C}_{19}\text{H}_{16}\text{DN}$: 260.1424, found: 260.1422 $[\text{M}]^+$. This compound has been reported already.^[11]



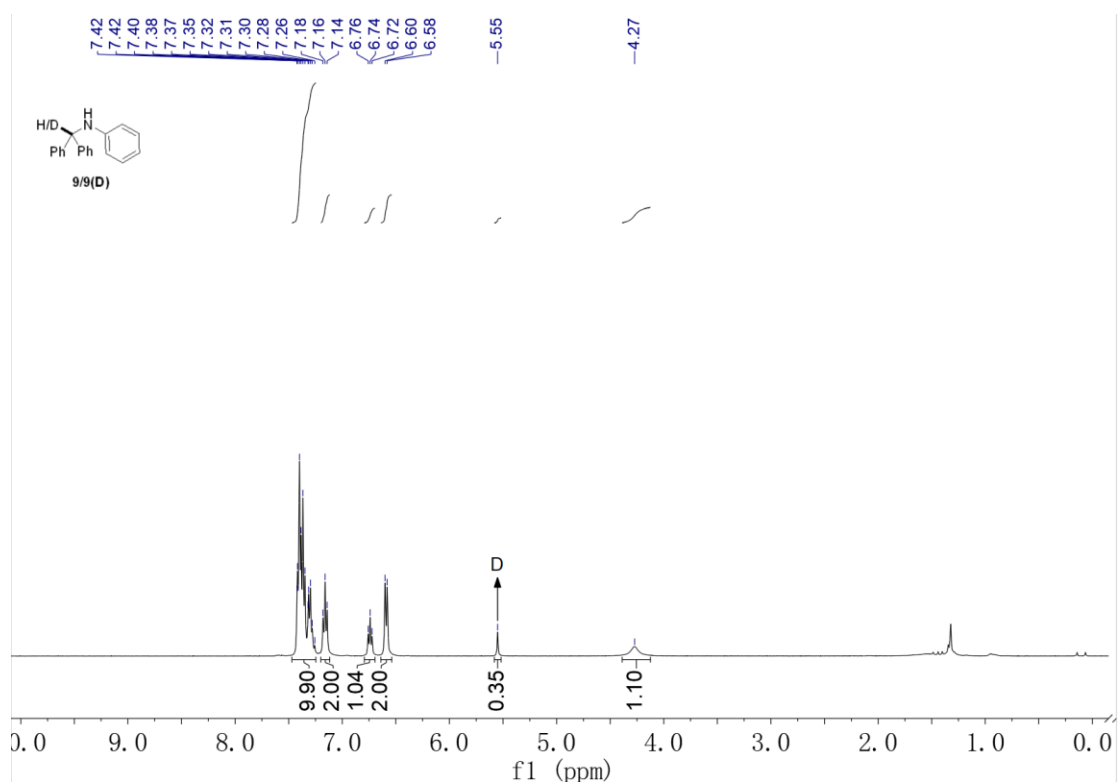


To an oven-dried Schlenk-tube equipped with magnetic stirring was treated with **1a** (51.4 mg, 0.2 mmol, 1.0 equiv), **2a** (90.4 mg, 0.4 mmol, 2.0 equiv), Cs₂CO₃ (29.3 mg, 0.09 mmol, 45 mol%), Ru(bpy)₃(PF₆)₂ (3.4 mg, 0.004 mmol, 2 mol%) and D₂O (7.2 μL, 0.4 mmol, 2.0 equiv). The Schlenk tube was put on vacuum and backfilled with nitrogen three times. Cy₂NMe (128 μL, 0.6 mmol, 3.0 equiv) and DMA (1 mL) were added in the Schlenk tube. The mixture was placed under a 30 W blue LED and stirred at ambient temperature. The reaction progress was monitored by TLC. Upon completion of the reaction, ethyl acetate was added to the mixture for extraction. The combined organic layer was dried with anhydrous Na₂SO₄ and evaporated under vacuum. The residue was purified by silica gel chromatography (eluted with petroleum ether/EtOAc = 30:1) to provide the product **3aa** (40.0 mg, 55%) and **9/9(D)** (13.0 mg, 25%, 60% D) as a white oil.

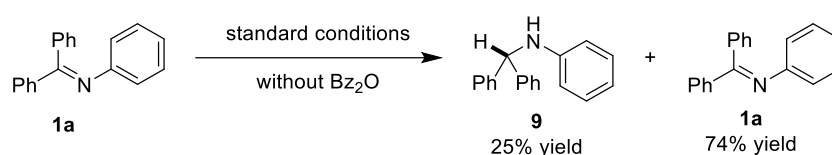




To an oven-dried Schlenk-tube equipped with magnetic stirring was treated with **1a** (51.4 mg, 0.2 mmol, 1.0 equiv), Ac₂O (38.0 μL, 0.4 mmol, 2.0 equiv), Cs₂CO₃ (29.3 mg, 0.09 mmol, 45 mol%), Ru(bpy)₃(PF₆)₂ (3.4 mg, 0.004 mmol, 2 mol%) and D₂O (7.2 μL, 0.4 mmol, 2.0 equiv). The Schlenk tube was put on vacuum and backfilled with nitrogen three times. Cy₂NMe (128 μL, 0.6 mmol, 3.0 equiv) and DMA (1 mL) were added in the Schlenk tube. The mixture was placed under a 30 W blue LED and stirred at ambient temperature. The reaction progress was monitored by TLC. Upon completion of the reaction, ethyl acetate was added to the mixture for extraction. The combined organic layer was dried with anhydrous Na₂SO₄ and evaporated under vacuum. The residue was purified by silica gel chromatography (eluted with petroleum ether/EtOAc = 30:1) to provide the product **9/9(D)** (37.9 mg, 73%, 65% D) as a white oil.

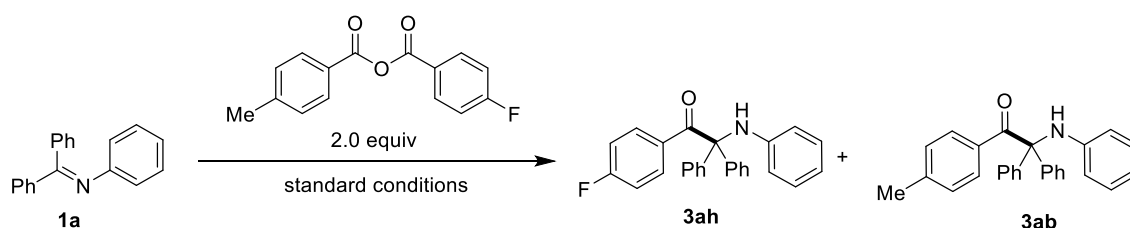


Reaction without Bz₂O

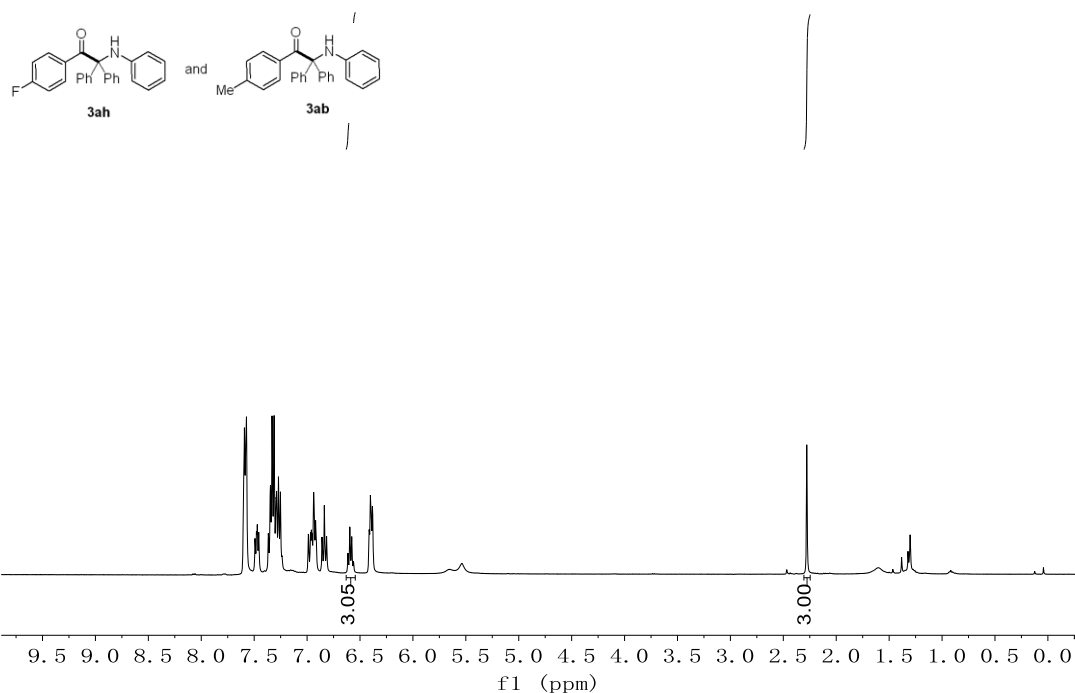


To an oven-dried Schlenk-tube equipped with magnetic stirring was treated with **1a** (51.4 mg, 0.2 mmol, 1.0 equiv), Cs₂CO₃ (29.3 mg, 0.09 mmol, 45 mol%) and Ru(bpy)₃(PF₆)₂ (3.4 mg, 0.004 mmol, 2 mol%). The Schlenk tube was put on vacuum and backfilled with nitrogen three times. Cy₂NMe (128 μL, 0.6 mmol, 3.0 equiv) and DMA (1 mL) were added in the Schlenk tube. The mixture was placed under a 30 W blue LED and stirred at ambient temperature. The reaction progress was monitored by TLC. Upon completion of the reaction, ethyl acetate was added to the mixture for extraction. The combined organic layer was dried with anhydrous Na₂SO₄ and evaporated under vacuum. The residue was purified by silica gel chromatography (eluted with petroleum ether/CH₂Cl₂ = 5:1) to provide the desired product **9** as a white oil (13.2 mg, 25%). This compound has been reported already.^[11]

Mixed anhydride selectivity experiment



To an oven-dried Schlenk-tube equipped with magnetic stirring was treated with **1a** (51.4 mg, 0.2 mmol, 1.0 equiv), mixed anhydride (145 mg, 0.4 mmol, 2.0 equiv), Cs₂CO₃ (29.3 mg, 0.09 mmol, 45 mol%), Ru(bpy)₃(PF₆)₂ (3.4 mg, 0.004 mmol, 2 mol%). The Schlenk tube was put on vacuum and backfilled with nitrogen three times. Cy₂NMe (128 μL, 0.6 mmol, 3.0 equiv) and DMA (1 mL) were added in the Schlenk tube. The mixture was placed under a 30 W blue LED and stirred at ambient temperature. The reaction progress was monitored by TLC. Upon completion of the reaction, ethyl acetate was added to the mixture for extraction. The combined organic layer was dried with anhydrous Na₂SO₄ and evaporated under vacuum. The residue was purified by silica gel chromatography (eluted with petroleum ether/EtOAc = 30:1) to provide the mixed product **3ah** and **3ab** (50.2 mg, **3ah:3ab** = 2:1) as a yellow solid. According to the NMR yield, **3ab** (16.5 mg, 22%), **3ah** (33.7mg, 44%).

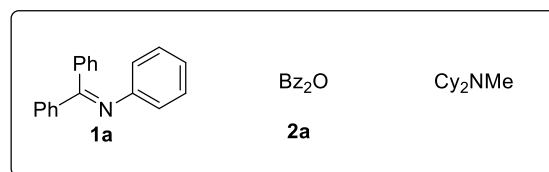


Stern-Volmer fluorescence quenching study

The rate of quenching (k_q) was determined using Stern-Volmer relationship:

$$\frac{I_0}{I} = K_q \times \tau_0 \times [\text{quencher}] + 1$$

Where I_0 is the fluorescence intensity without the quencher, I is the fluorescence intensity with the quencher, and τ_0 is the lifetime of the photoexcited state of the photocatalyst. The excited state lifetime of $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ in MeCN is 153 ns^[14]. In this study the compounds below are tested.



Evaluation of 1a as potential quencher for photoexcited $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$

$\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ (1.72 mg, 0.002 mmol) was dissolved in 2.0 mL DMA to prepare a 0.001 M solution. 50 μL of this solution and DMA (2.0 mL) were added to each of a set of 7 cuvettes. Subsequently, the solution of quencher **1a** in DMA (3.0 mL, 0.01 M) was added in increasing amounts (0, 100 μL , 200 μL , 300 μL , 500 μL , 800 μL , 1200 μL) to the cuvette. All solutions were excited at 450 nm and the fluorescence emission was

detected at 600 nm. The ratio of the maximum fluorescence emission intensities maximum between samples without and with quencher were plotted against the quencher concentration to generate the Stern-Volmer plots below.

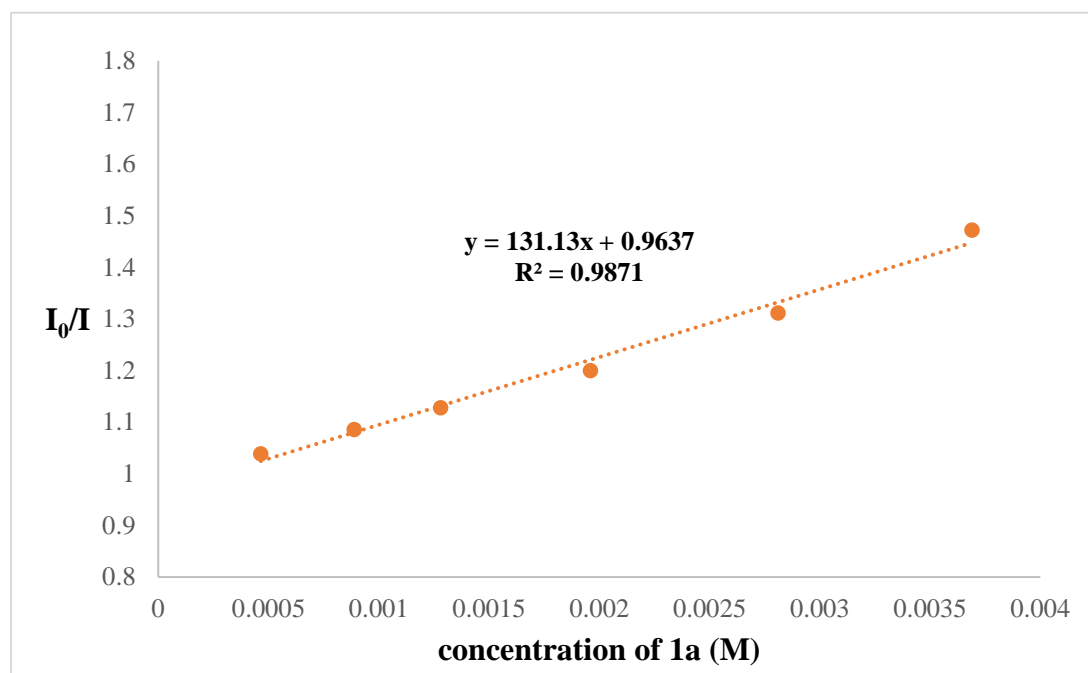


Figure S2. Stern-Volmer quenching experiment of $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ and **1a**. k_q is $8.6 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$.

Evaluation of **2a as potential quencher for photoexcited $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$**

$\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ (1.72 mg, 0.002 mmol) was dissolved in 2.0 mL DMA to prepare a 0.001 M solution. 50 μL of this solution and DMA (2.0 mL) were added to each of a set of 7 cuvettes. Subsequently, the solution of quencher **2a** in DMA (3.0 mL, 0.01 M) was added in increasing amounts (0, 100 μL , 200 μL , 300 μL , 500 μL , 800 μL , 1200 μL) to the cuvette. All solutions were excited at 450 nm and the fluorescence emission was detected at 600 nm. The ratio of the maximum fluorescence emission intensities maximum between samples without and with quencher were plotted against the quencher concentration to generate the Stern-Volmer plots below.

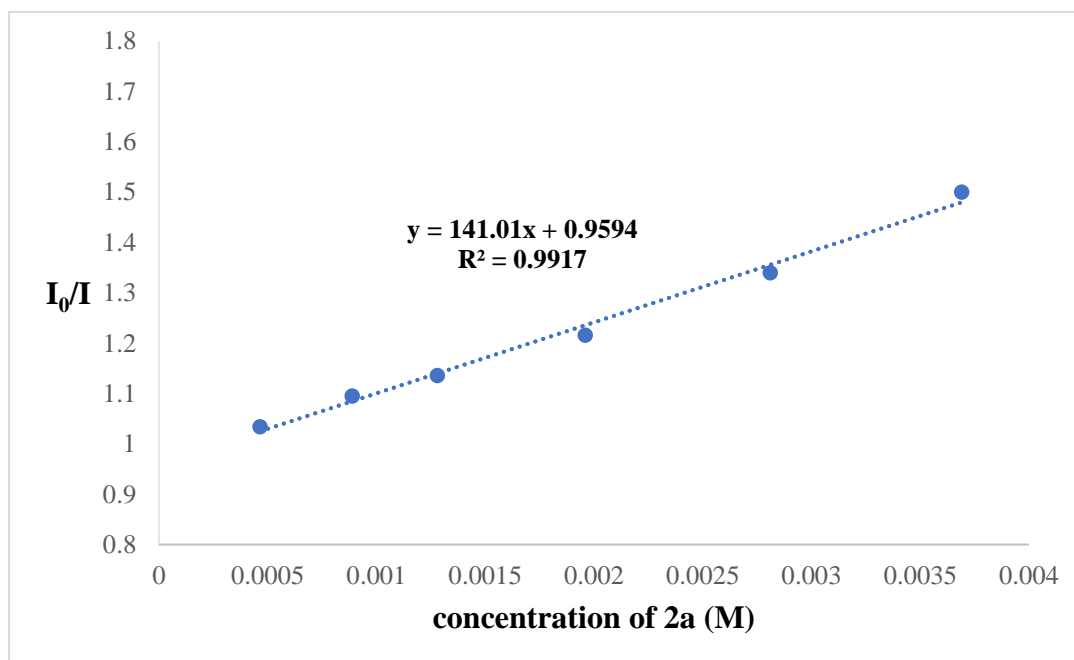


Figure S3. Stern-Volmer quenching experiment of Ru(bpy)₃(PF₆)₂ and **2a**. k_q is $9.2 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$.

Evaluation of Cy₂NMe as potential quencher for photoexcited Ru(bpy)₃(PF₆)₂

Ru(bpy)₃(PF₆)₂ (1.72 mg, 0.002 mmol) was dissolved in 2.0 mL DMA to prepare a 0.001 M solution. 50 μL of this solution and DMA (2.0 mL) were added to each of a set of 7 cuvettes. Subsequently, the solution of quencher Cy₂NMe in DMA (3.0 mL, 0.01 M) was added in increasing amounts (0, 100 μL, 200 μL, 300 μL, 500 μL, 800 μL, 1200 μL) to the cuvette. All solutions were excited at 450 nm and the fluorescence emission was detected at 600 nm. The ratio of the maximum fluorescence emission intensities maximum between samples without and with quencher were plotted against the quencher concentration to generate the Stern-Volmer plots below.

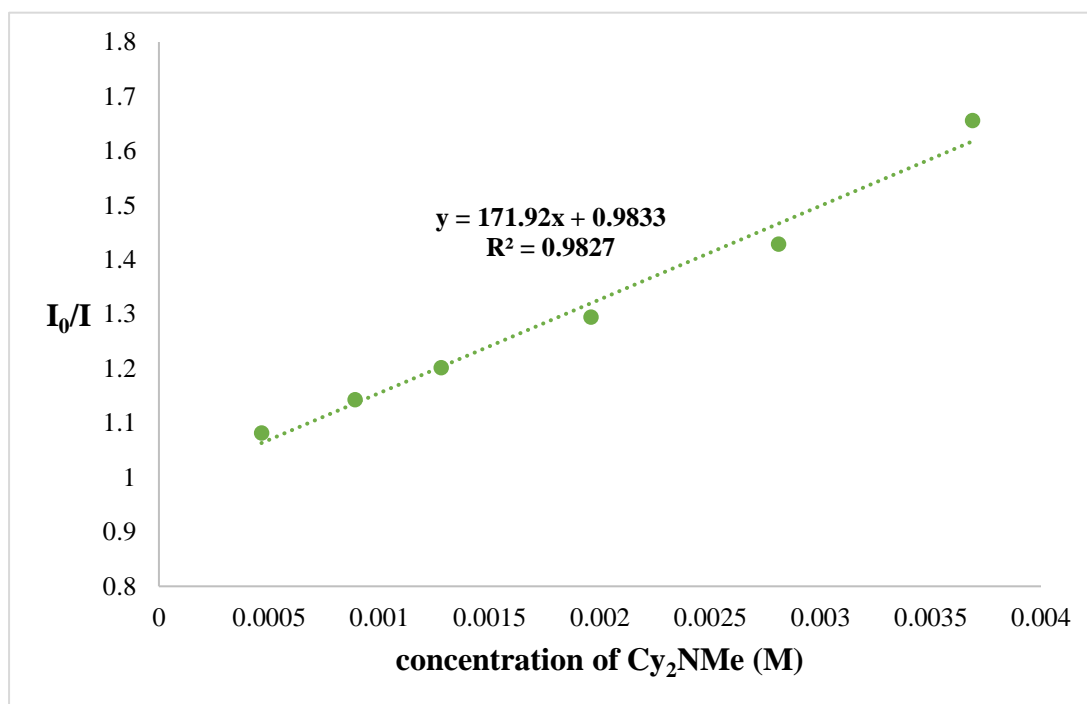


Figure S4. Stern-Volmer quenching experiment of $Ru(bpy)_3(PF_6)_2$ and Cy_2NMe . k_q is $1.1 \times 10^9 M^{-1}s^{-1}$.

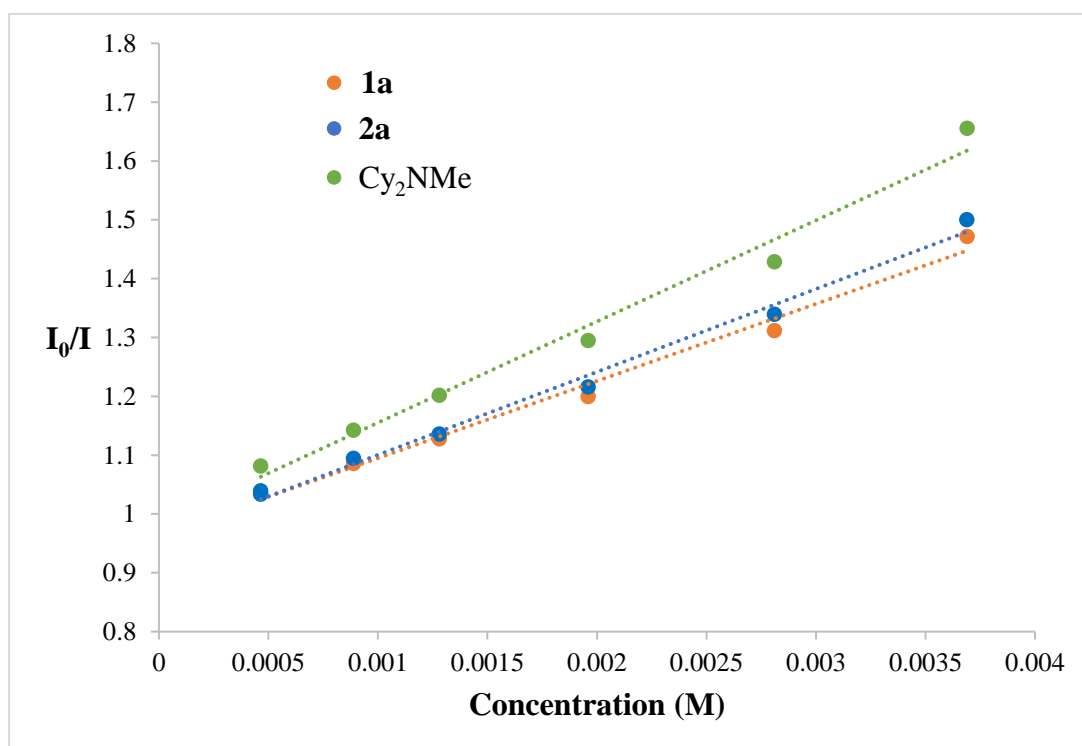


Figure S5. The overlap of all the Stern-Volmer quenching experiments.

Plausible mechanism pathway B

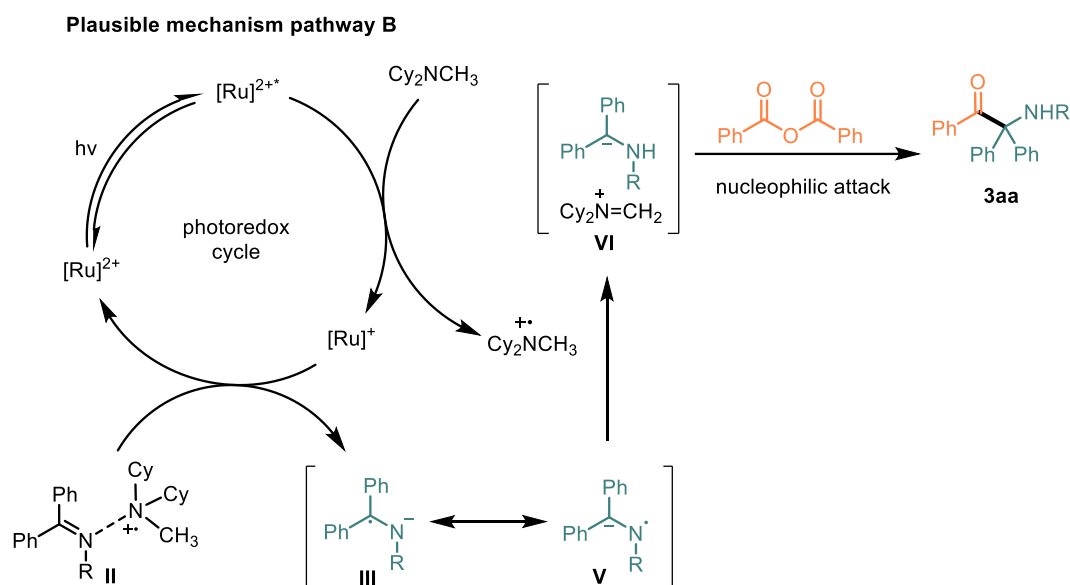


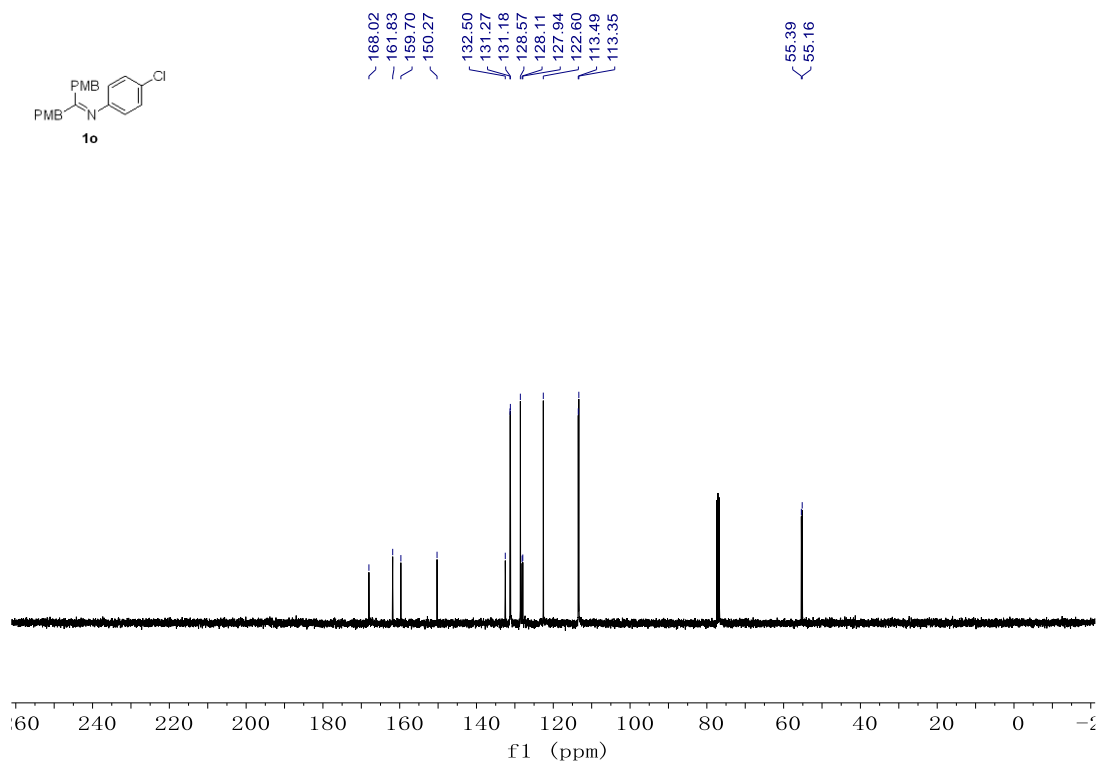
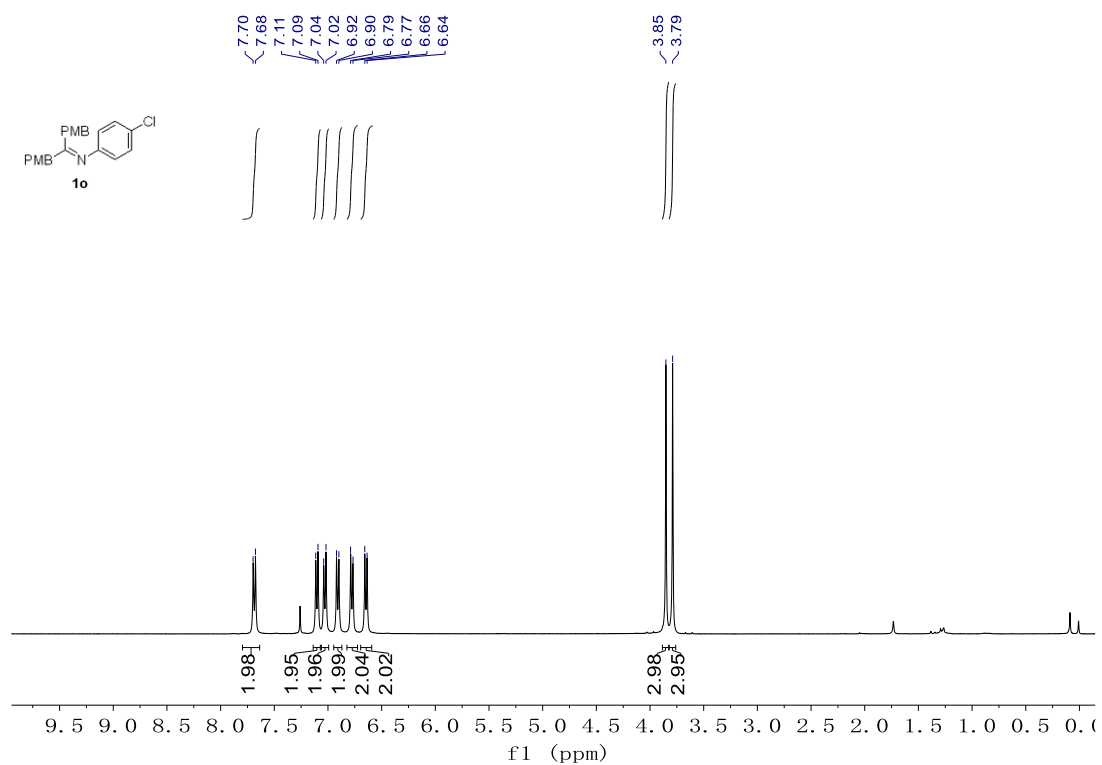
Figure S6. Carbanion nucleophilic mechanism pathway

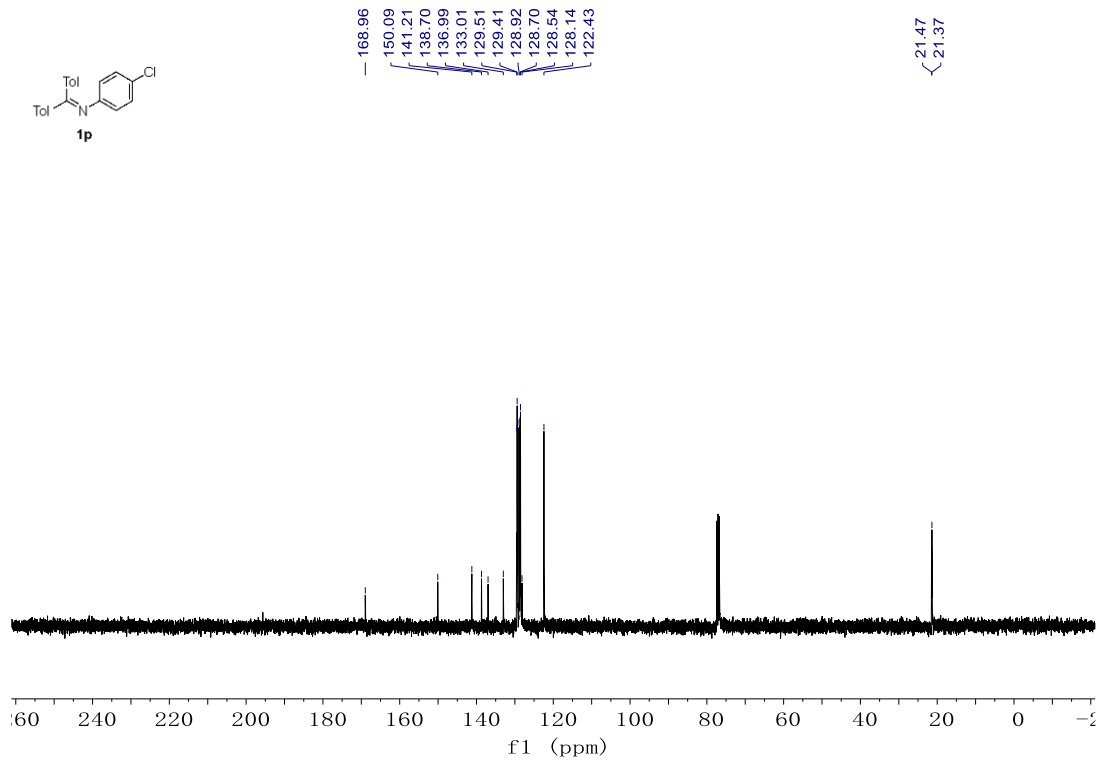
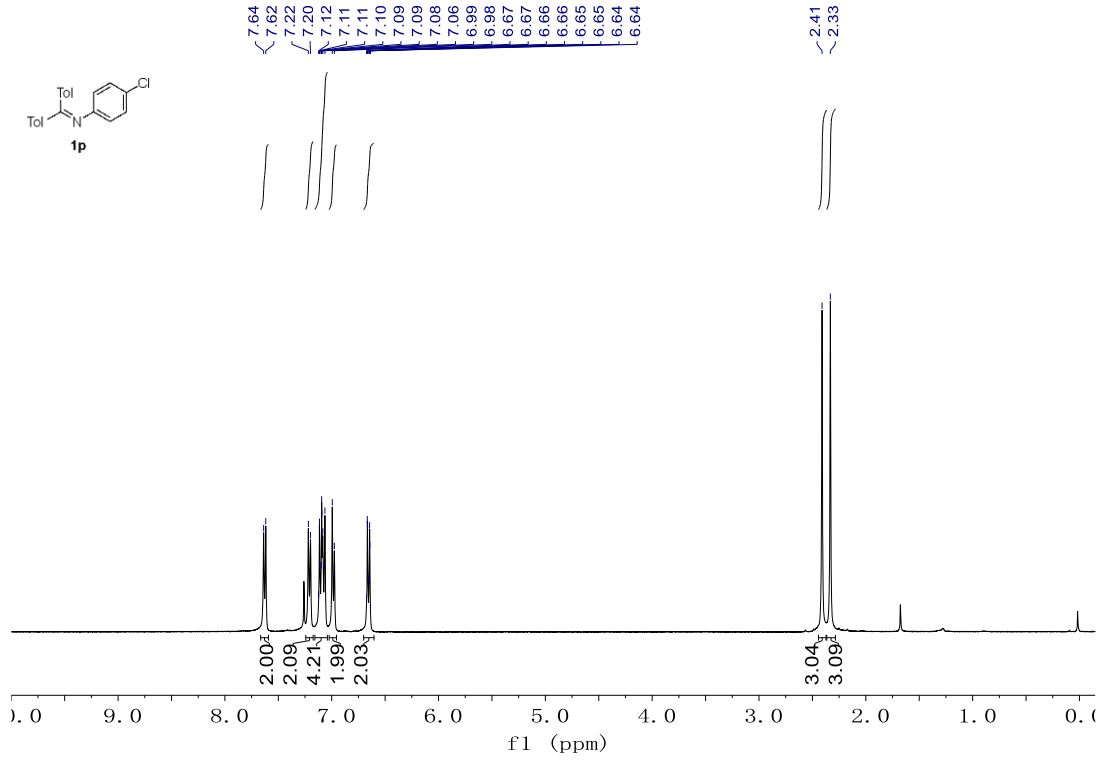
Under the irradiation of blue LEDs, the excited photocatalyst $[Ru]^{2+*}$ was quenched by the sacrificial Cy_2NCH_3 to form the reduced state $[Ru]^+$ ($E_{1/2}^{II^*/I} = 0.77$ V vs. SCE)^[15] and $[Cy_2NCH_3]^{+\bullet}$. imine **1a** was activated by the amine radical cation, $[Cy_2NCH_3]^{+\bullet}$, to form a 2-center-3-electron **II**, which subsequently underwent a reduction by $[Ru]^+$ via SET process, affording the α -amino radical anion **III/V** and regenerating the ground state photocatalyst $[Ru]^{2+}$ ($E_{1/2}^{I/II} = -1.33$ V vs. SCE).^[15] Due to the high reactivity of the N-centered radical,^[11] **V** was instantaneously quenched by $[Cy_2NCH_3]^{+\bullet}$ via HAT process to form α -amino carbanion **VI**. Finally, α -amino carbanion **VI** attacked the anhydride via nucleophilic addition, affording the desired α -amino ketone **3aa**.

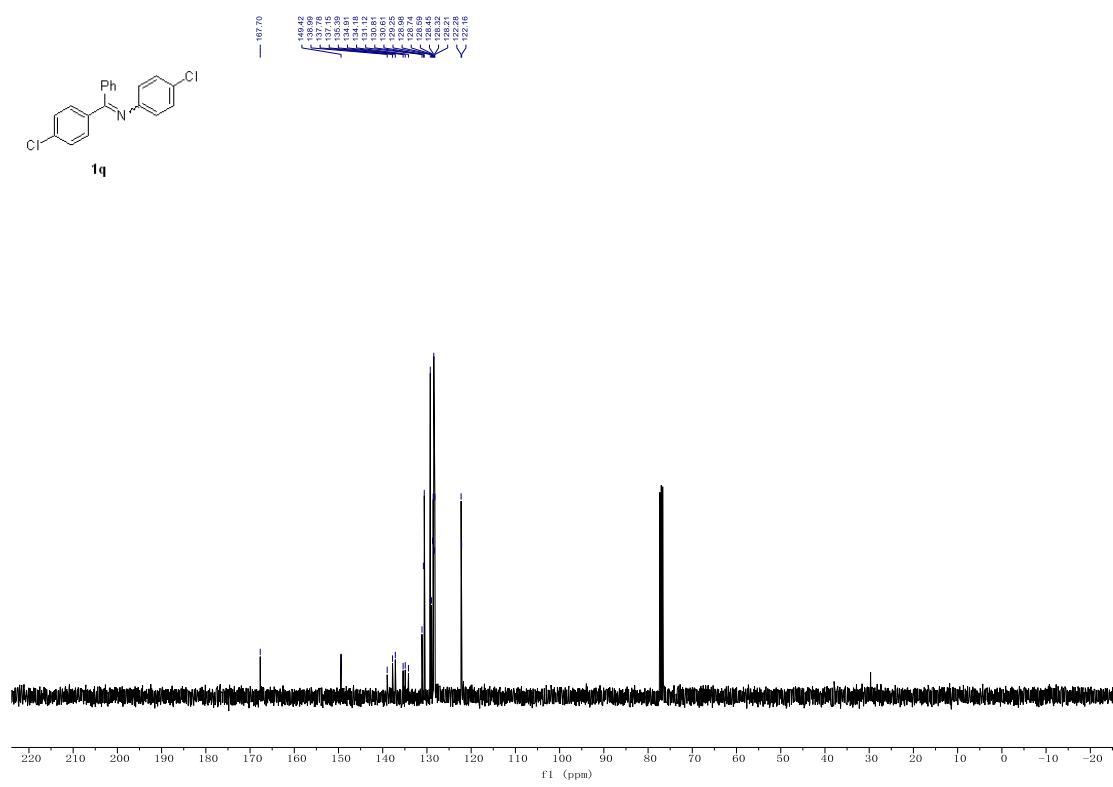
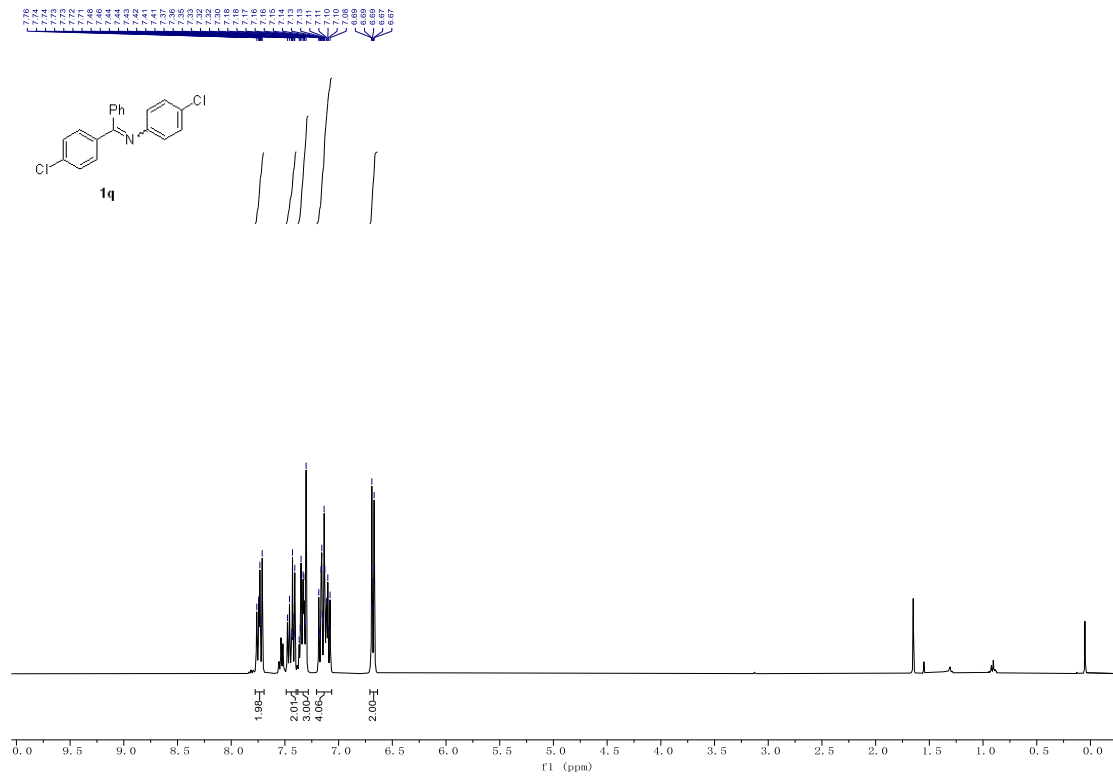
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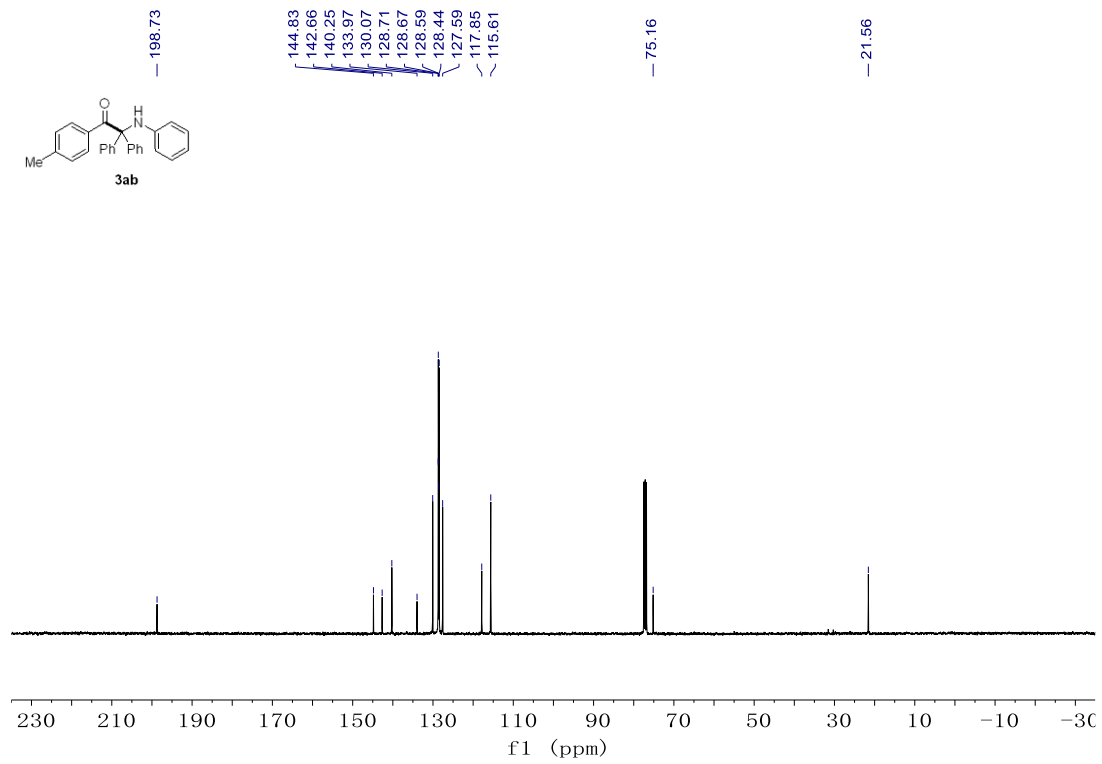
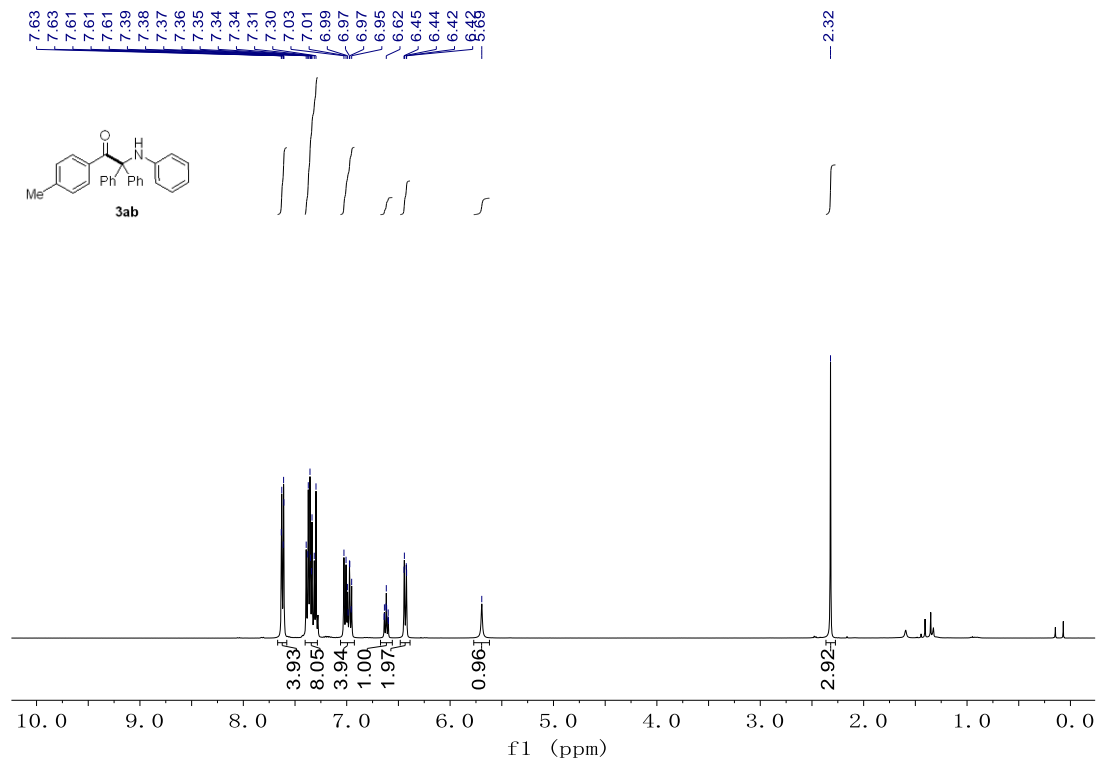
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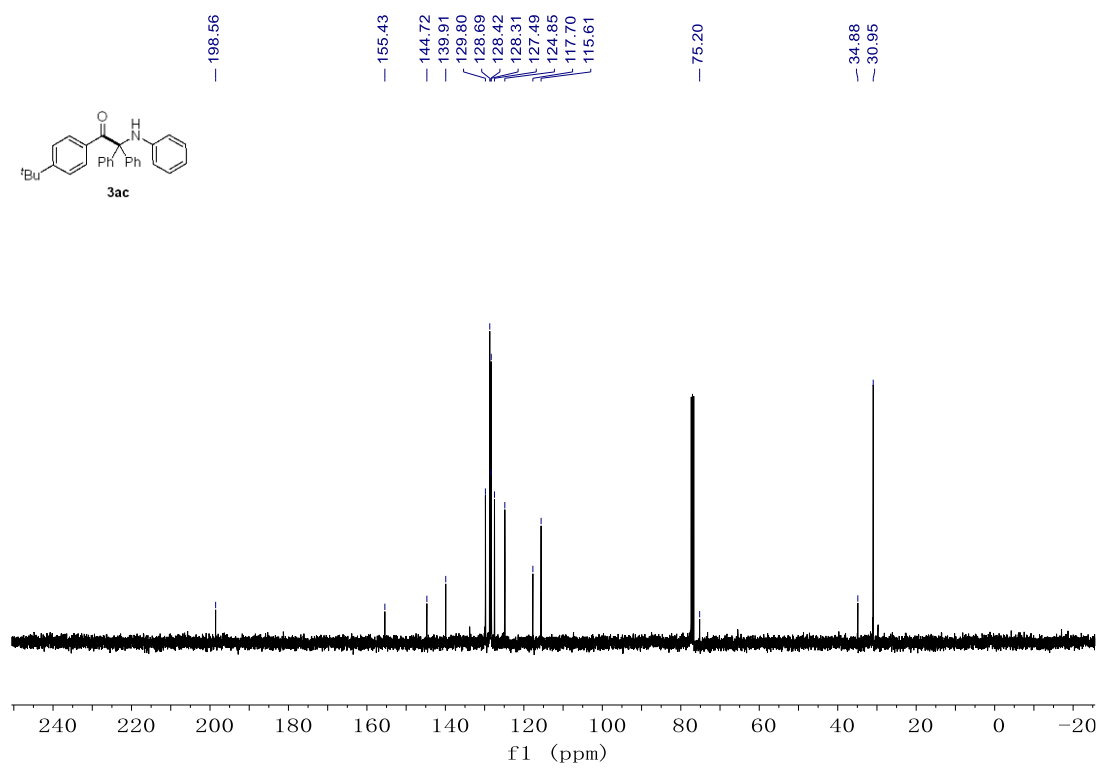
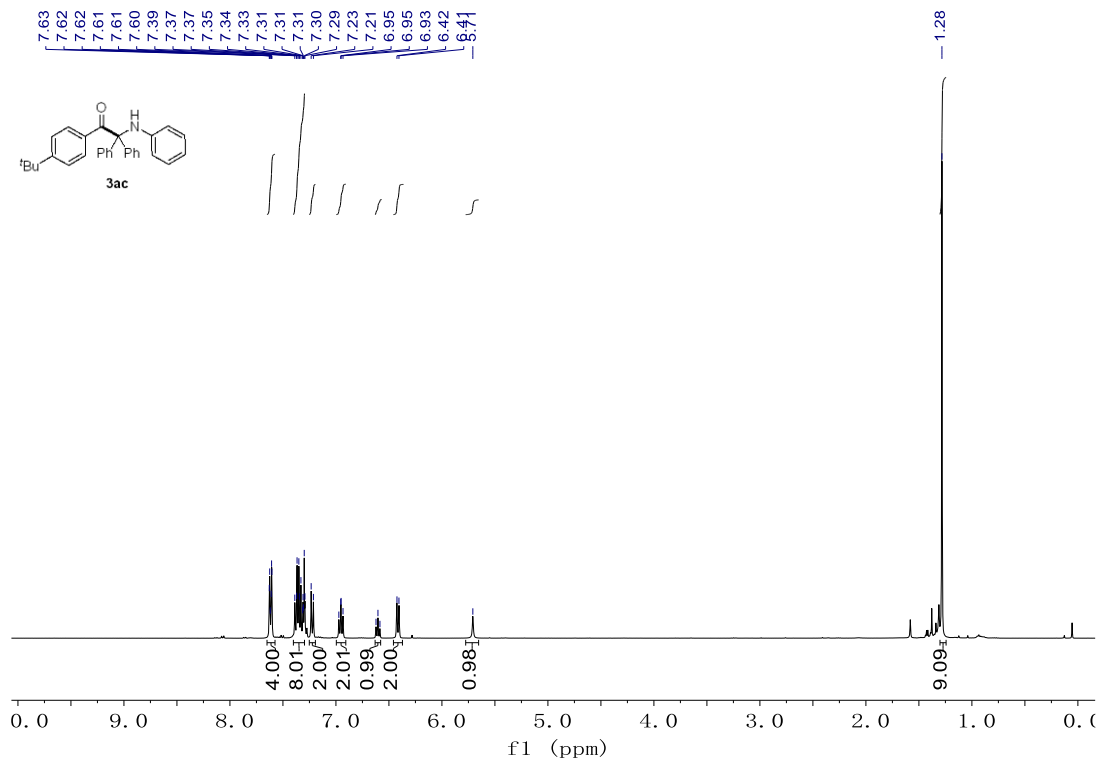
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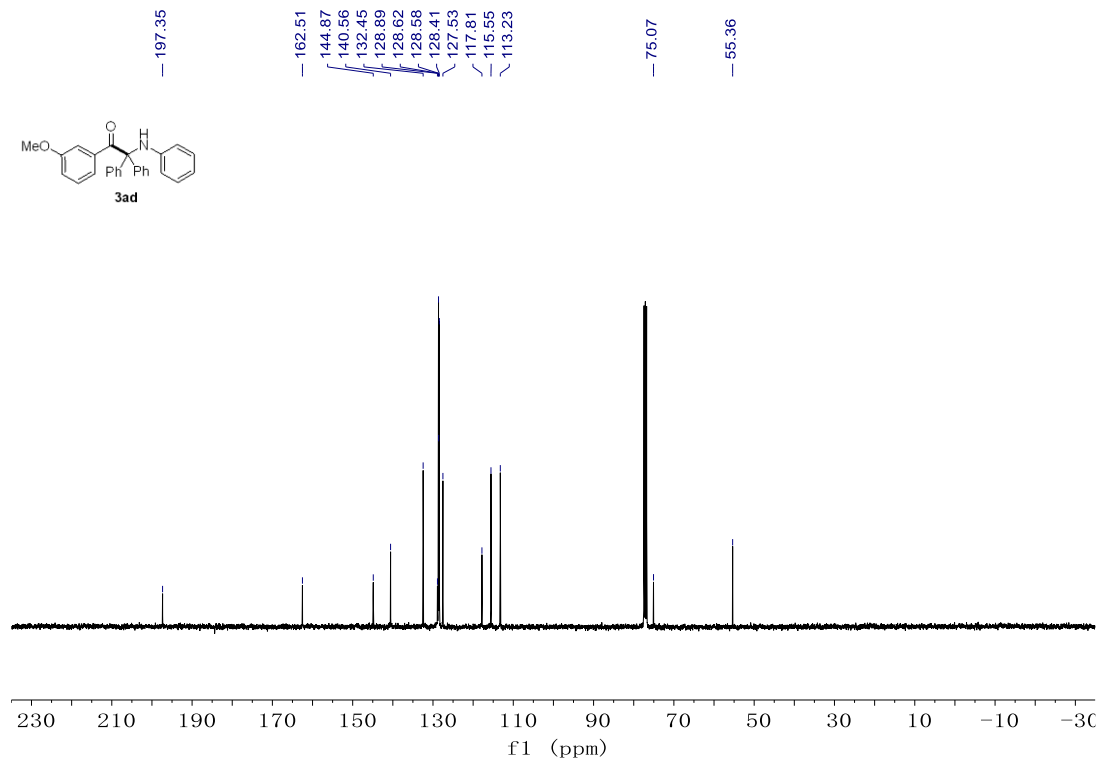
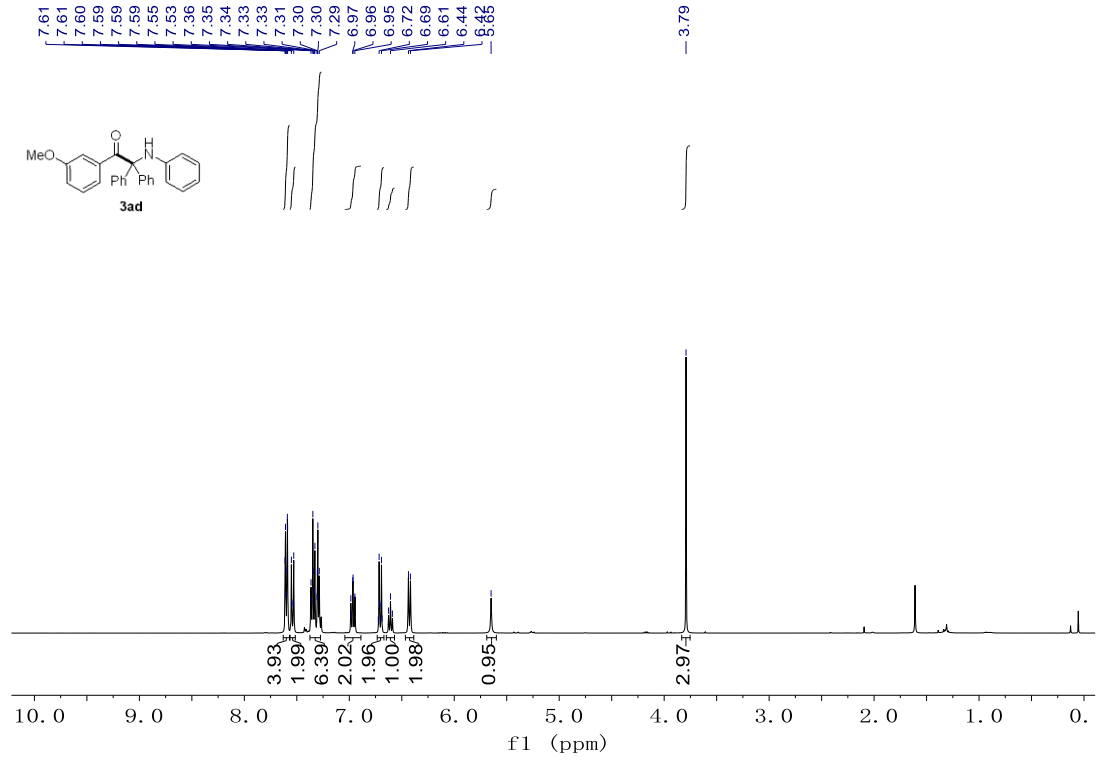


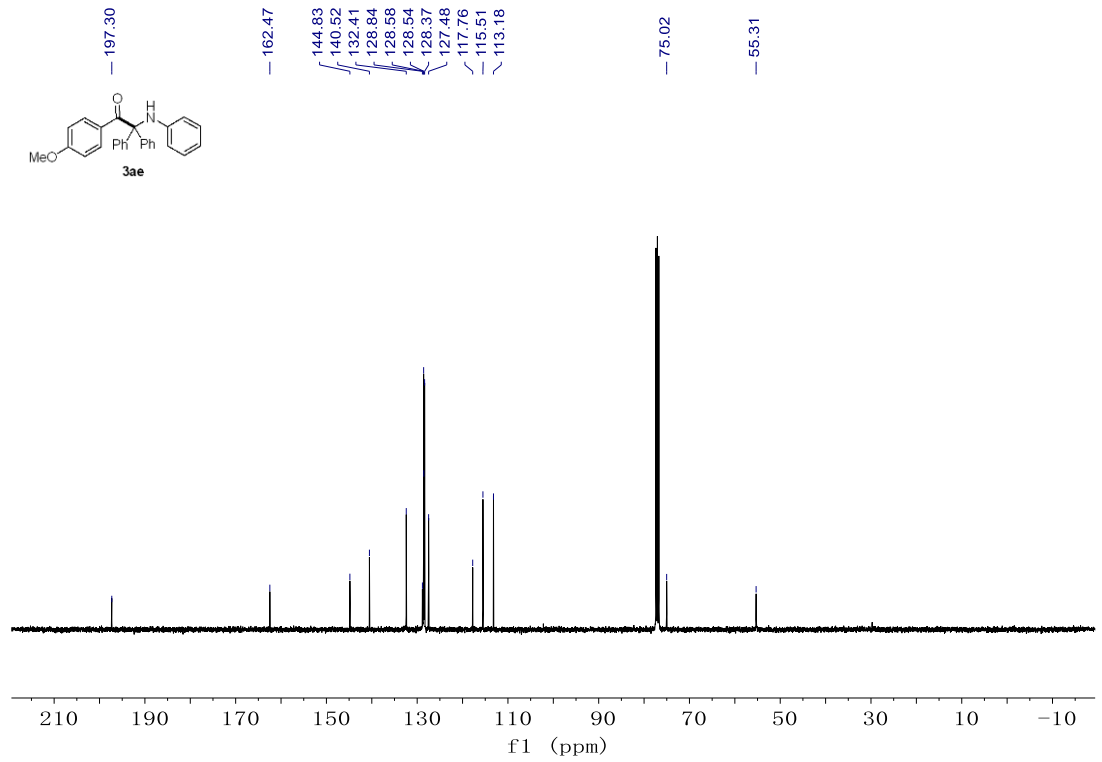
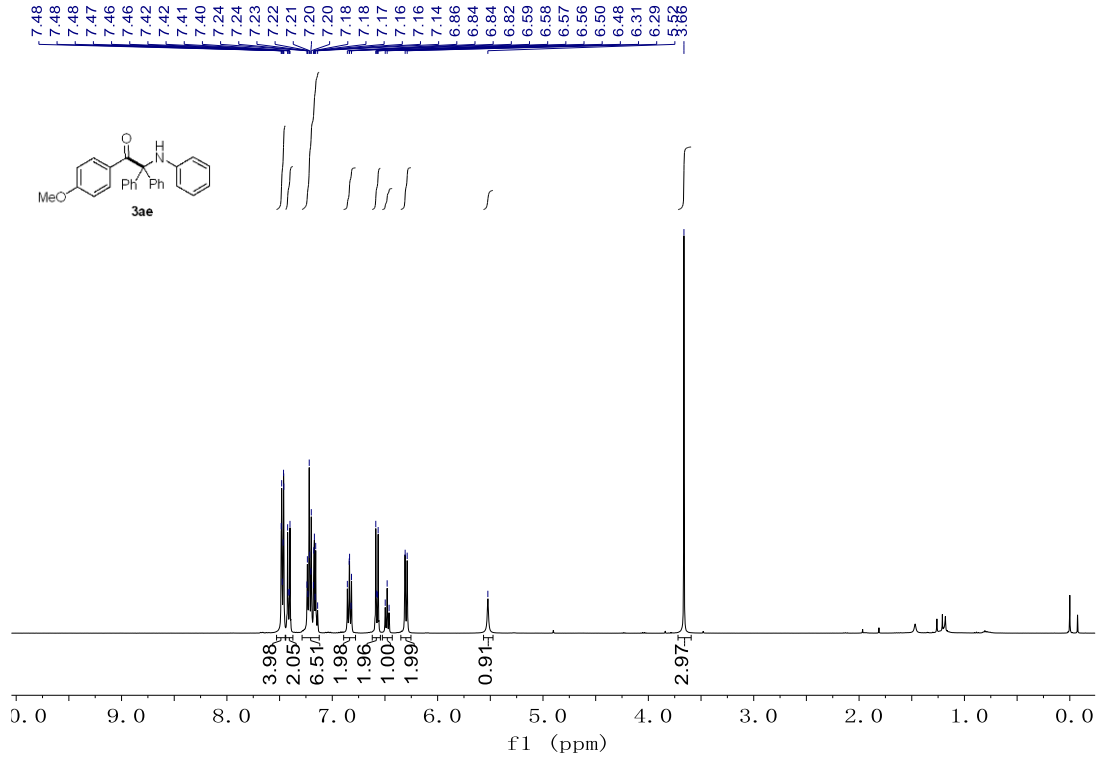


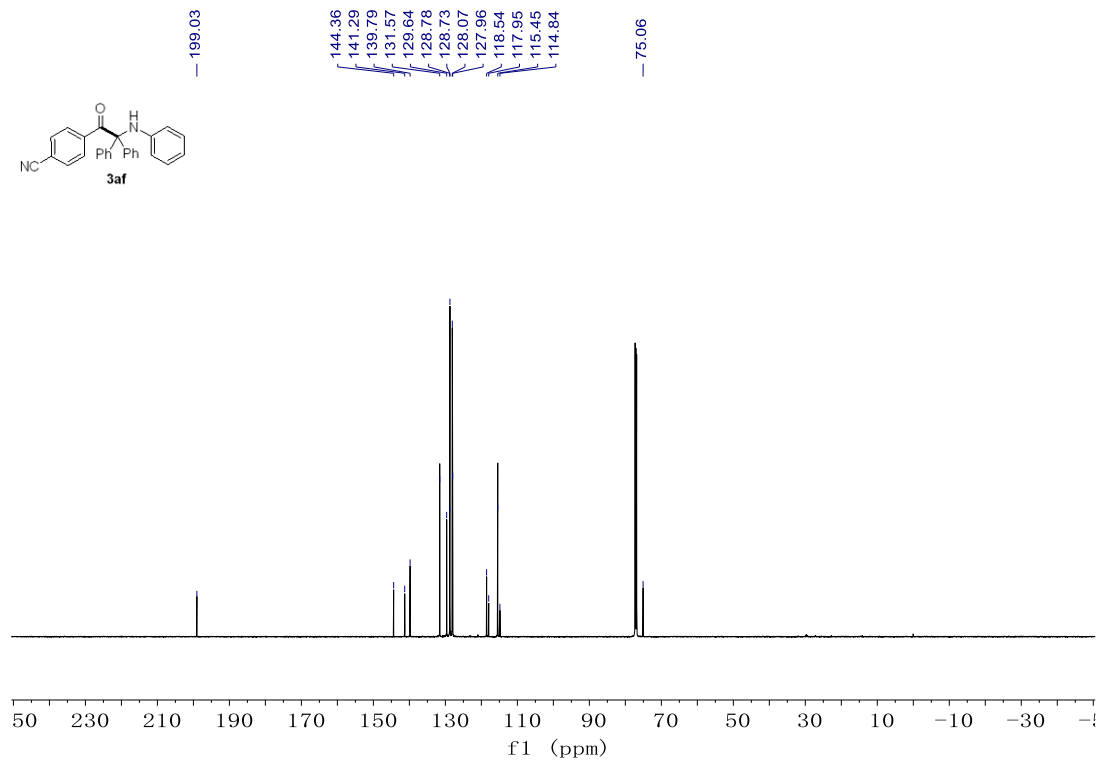
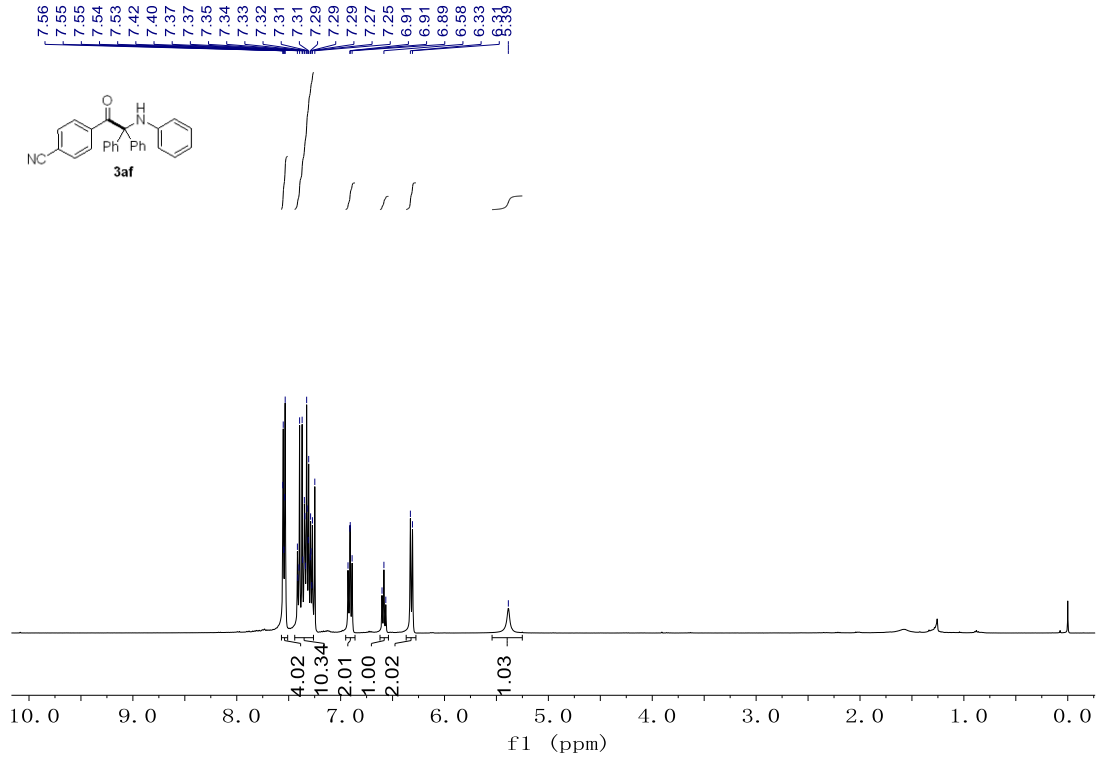


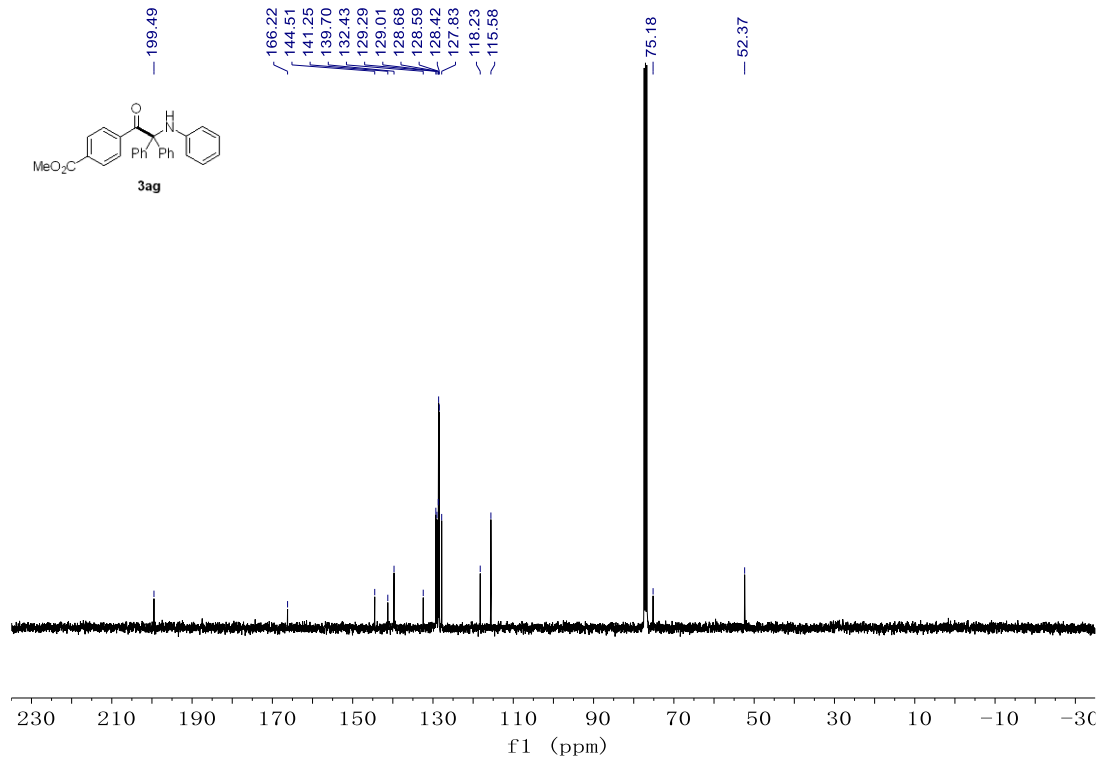
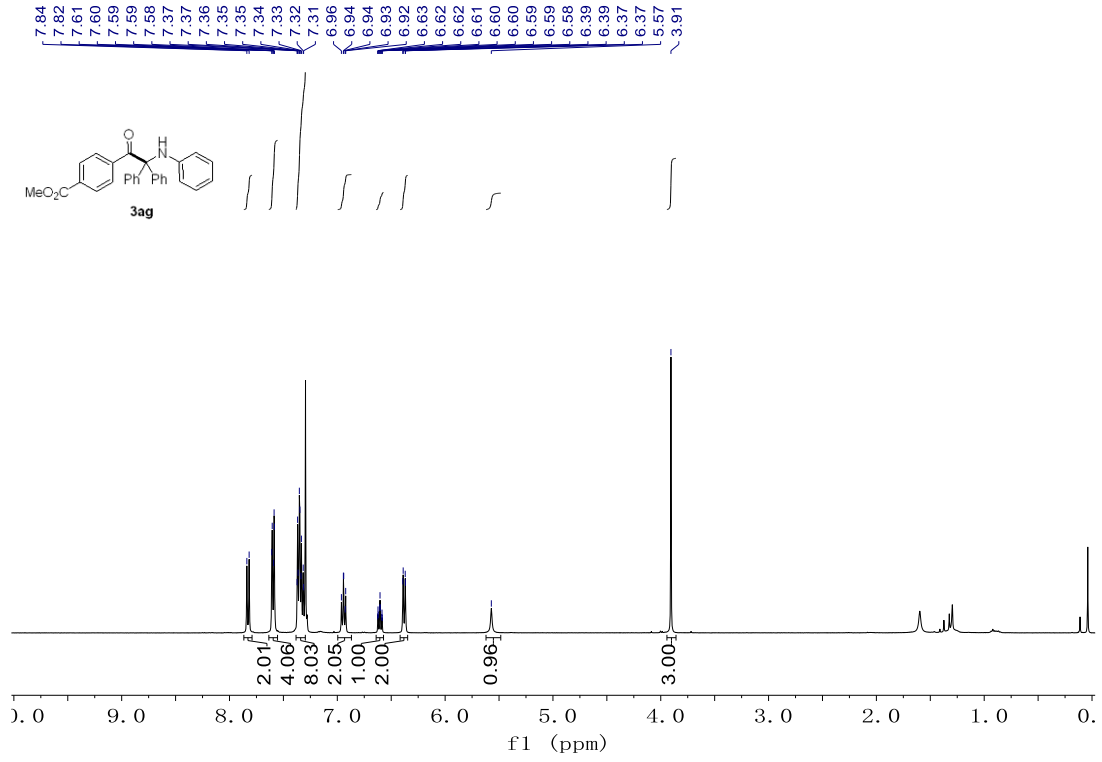


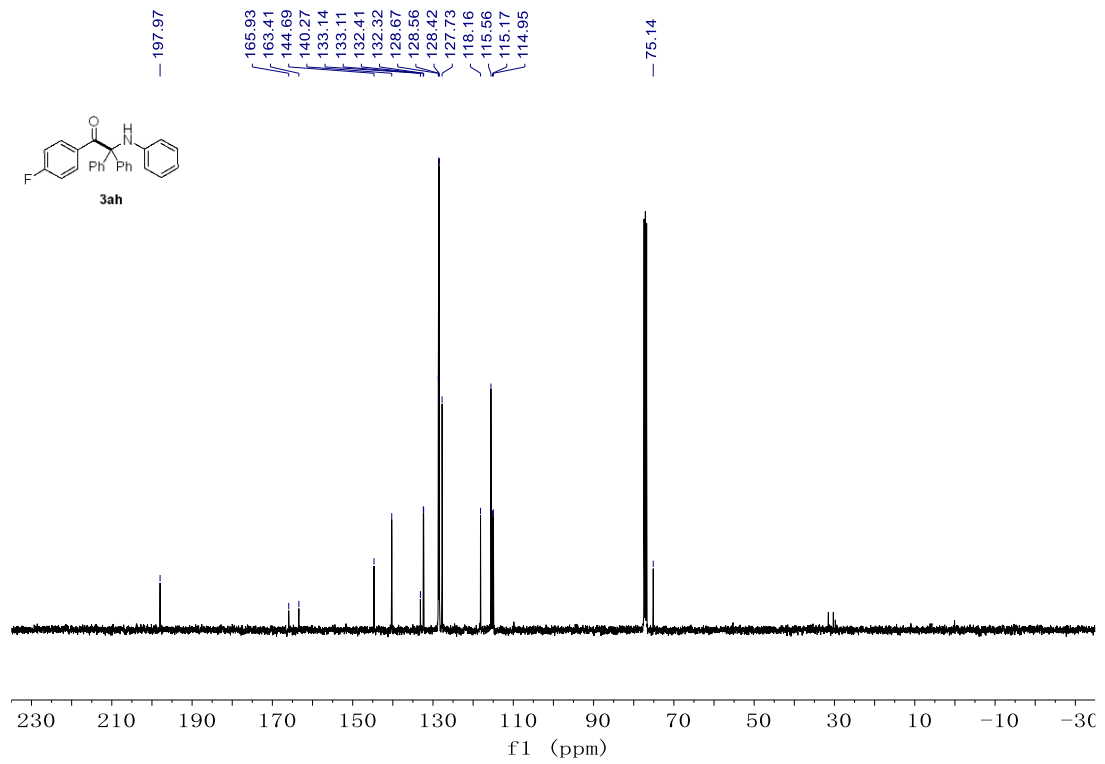
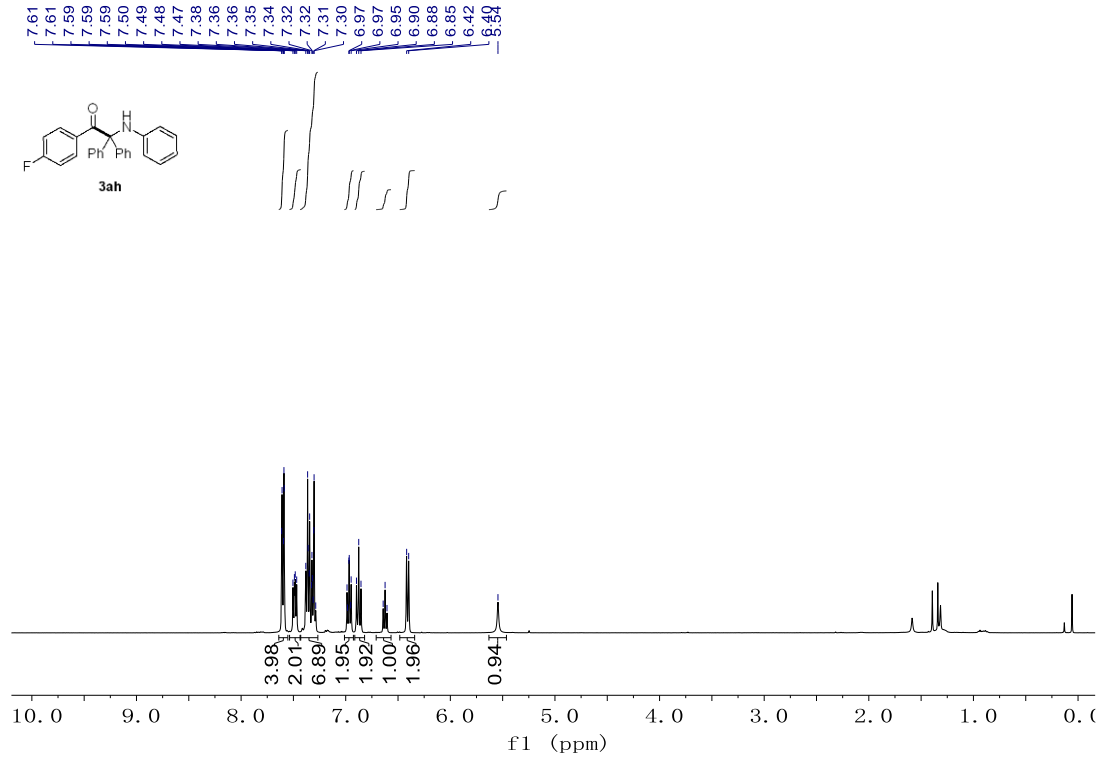


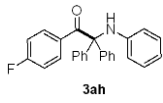




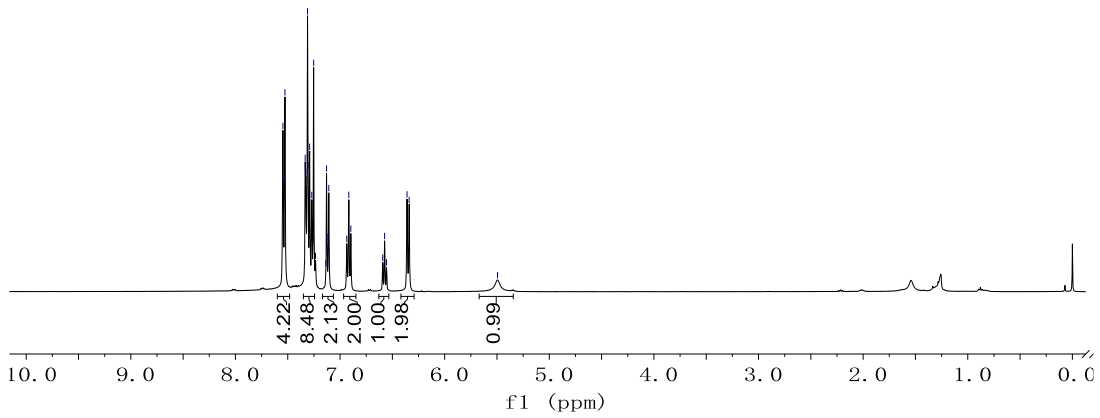
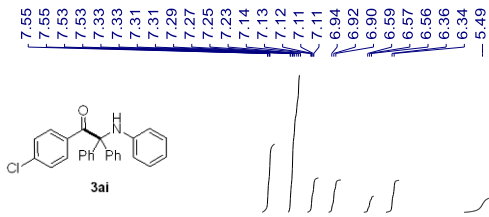
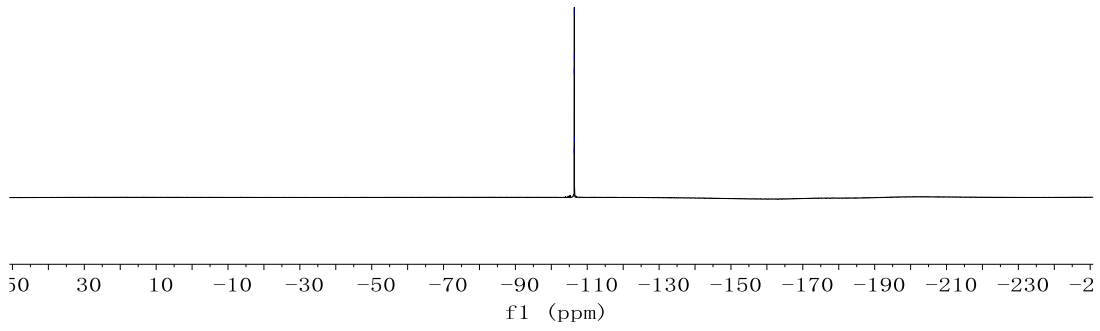


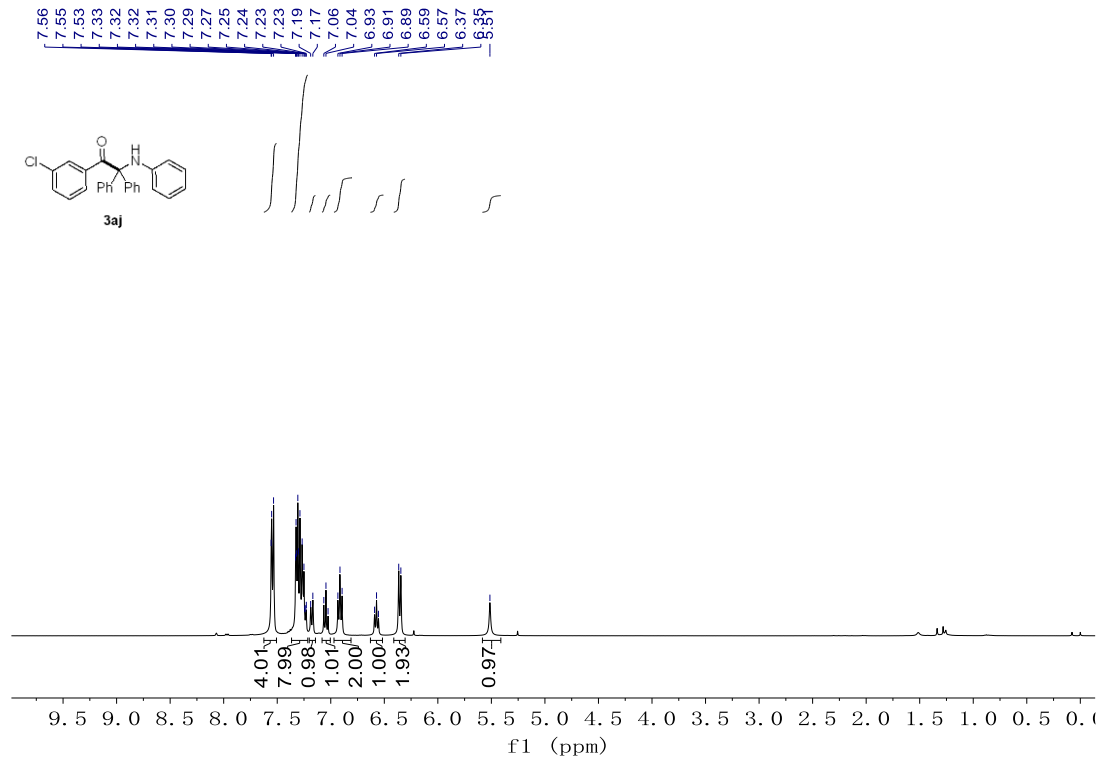
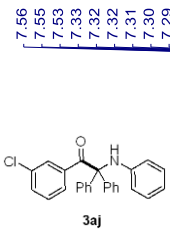
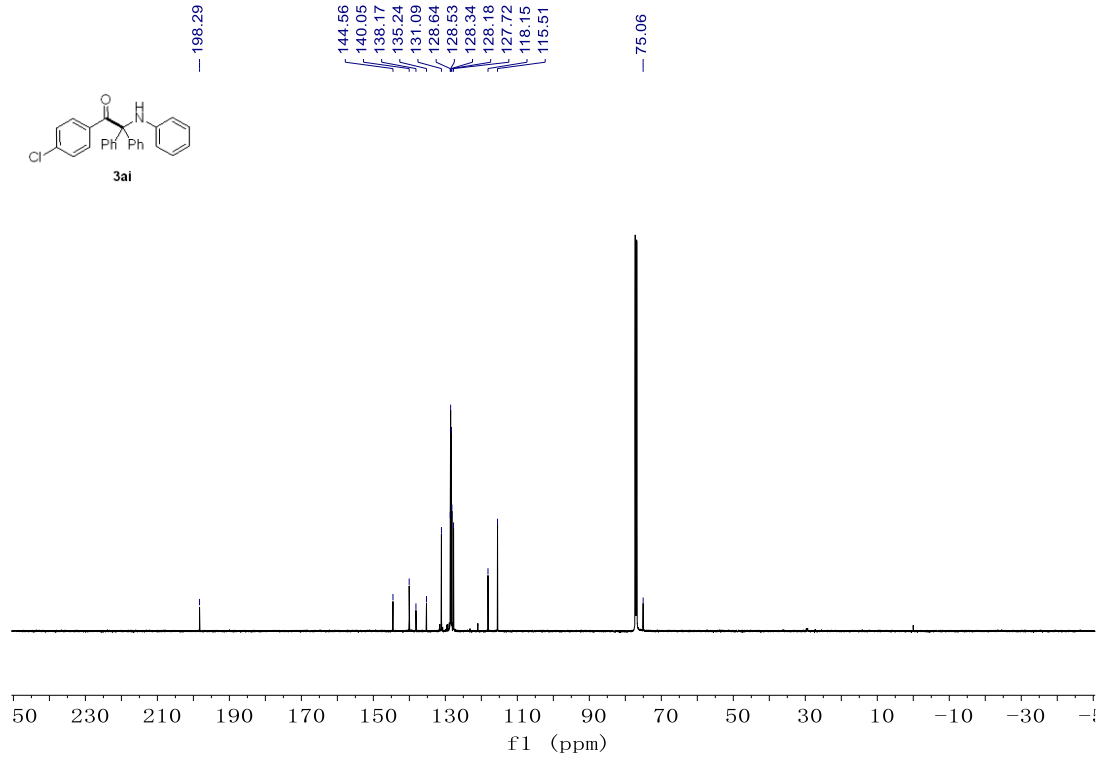
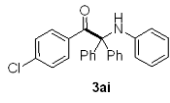


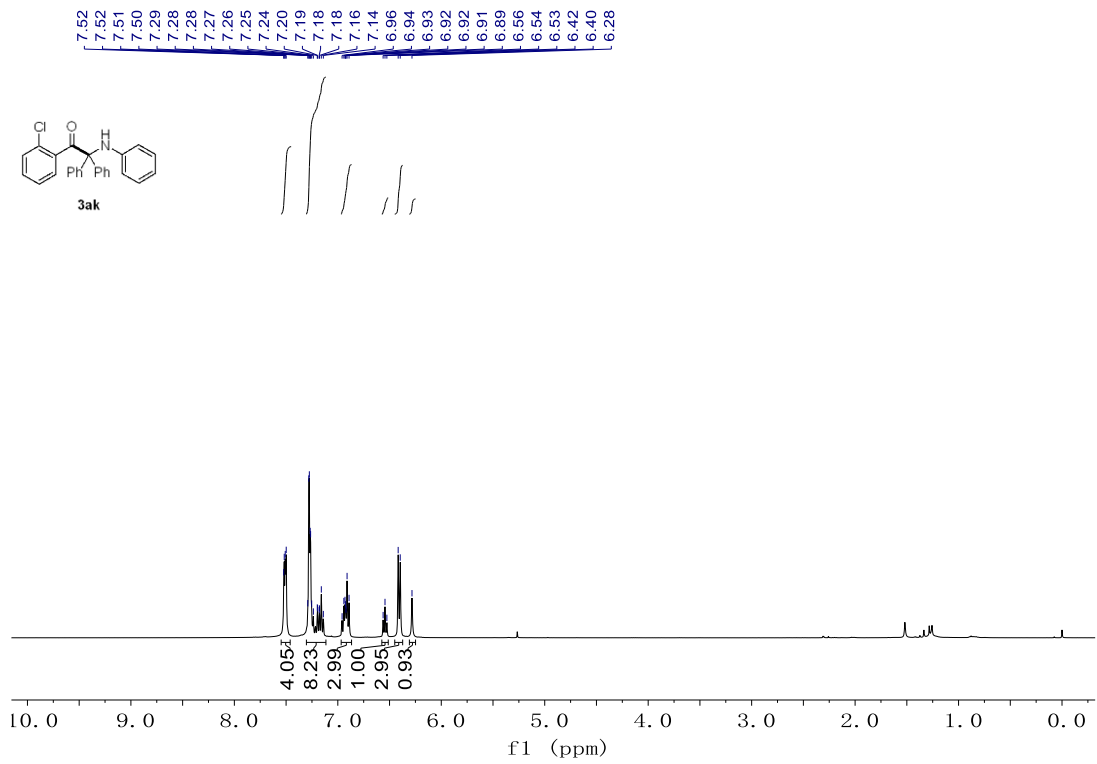
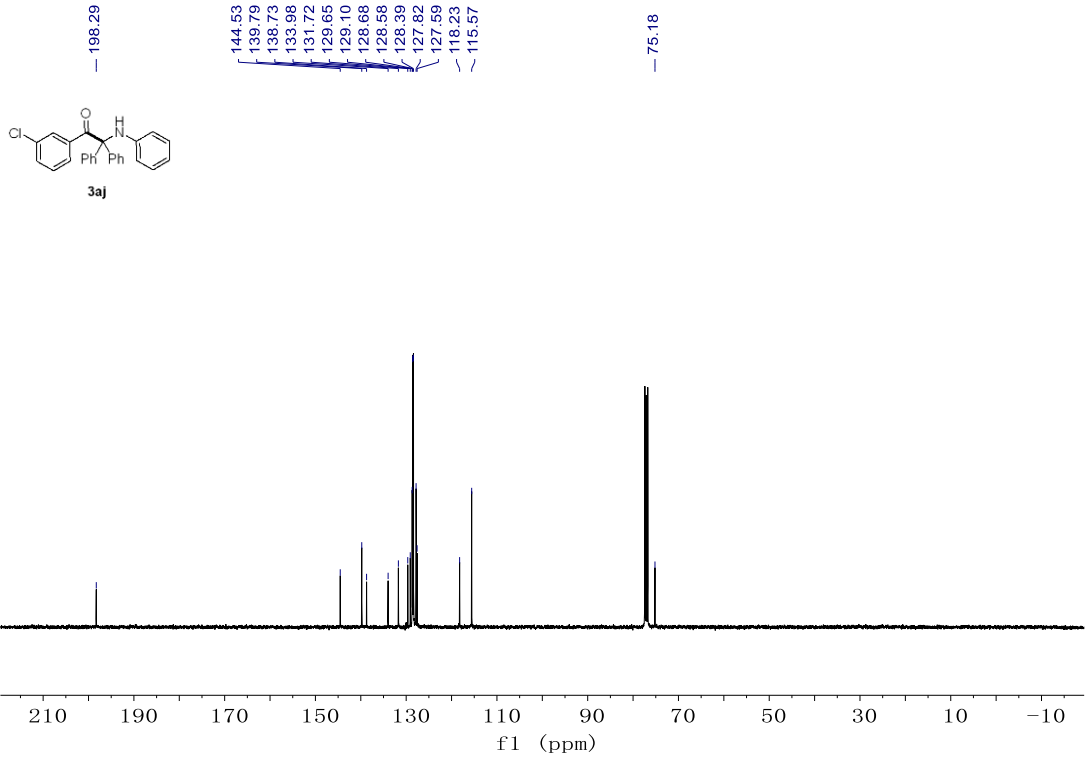


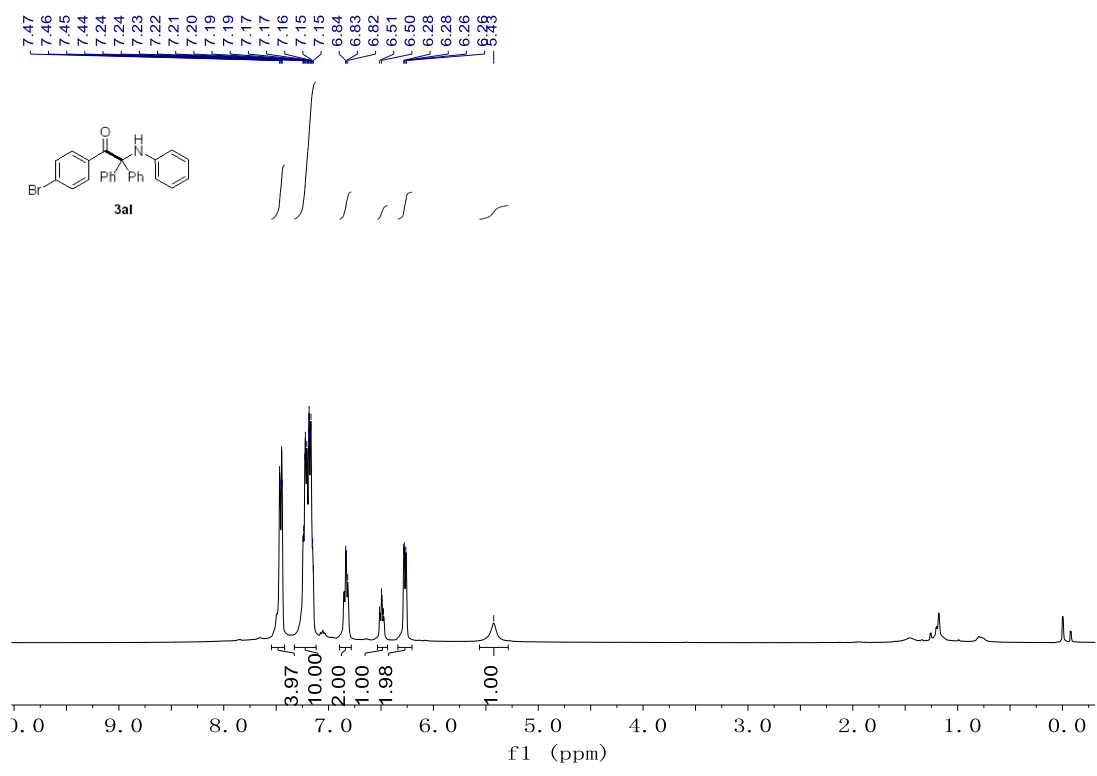
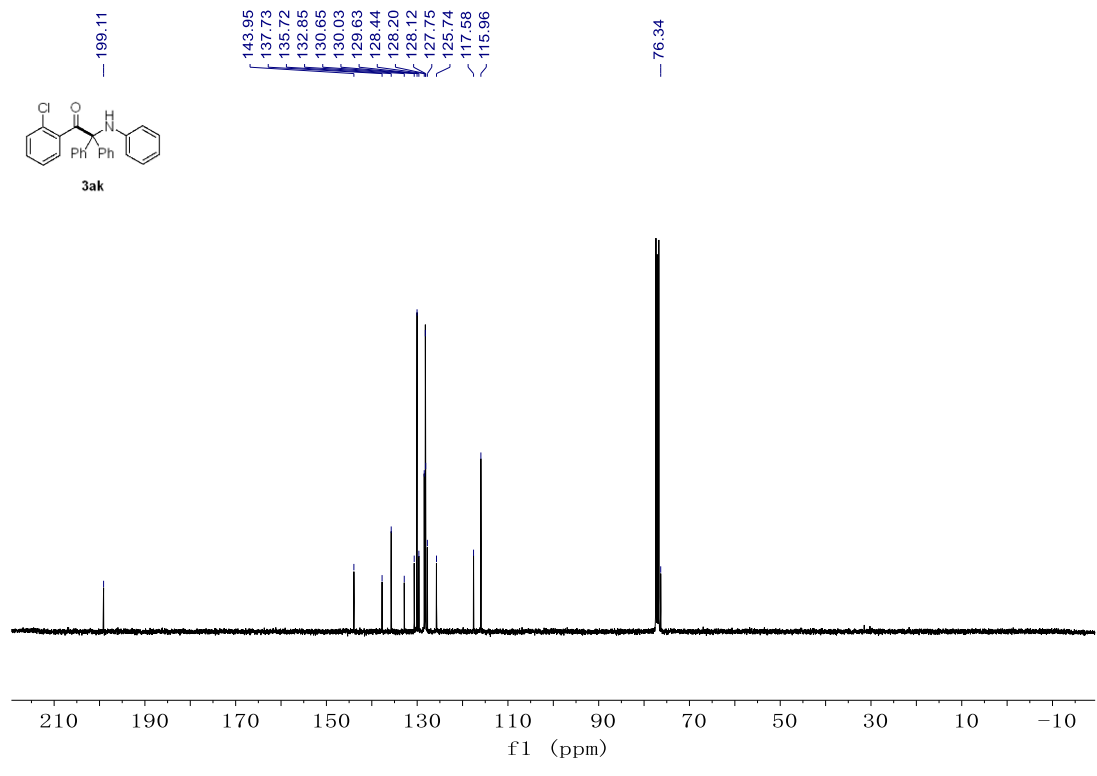


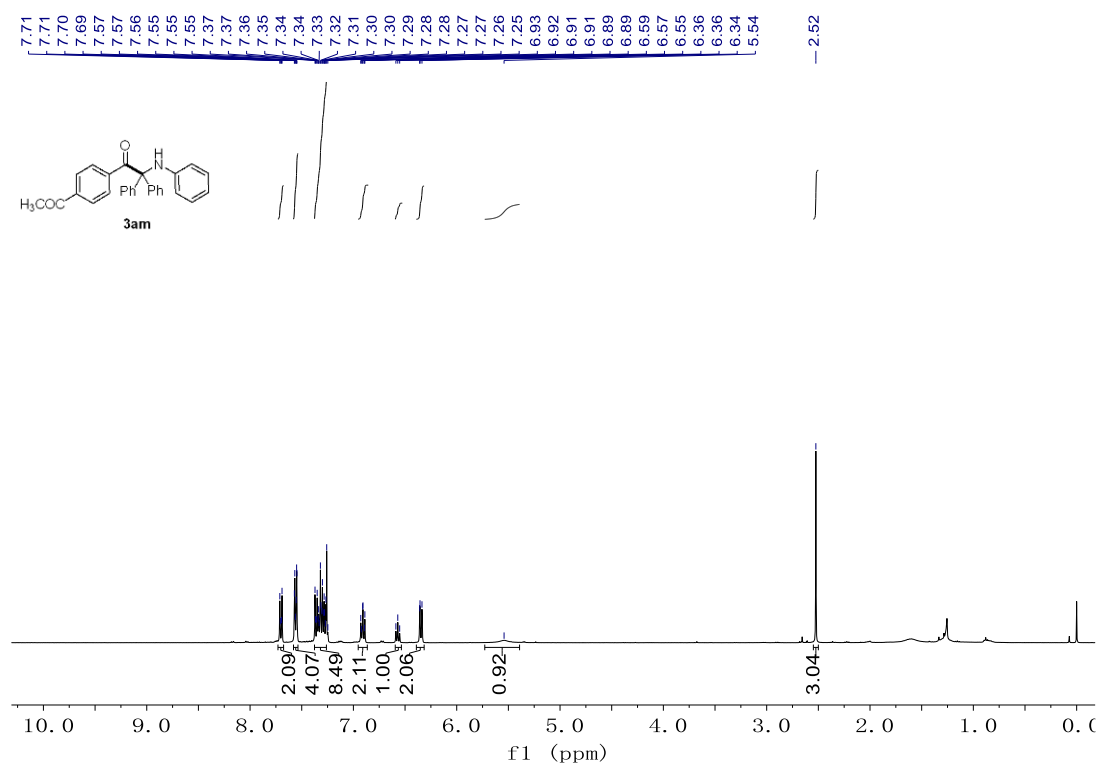
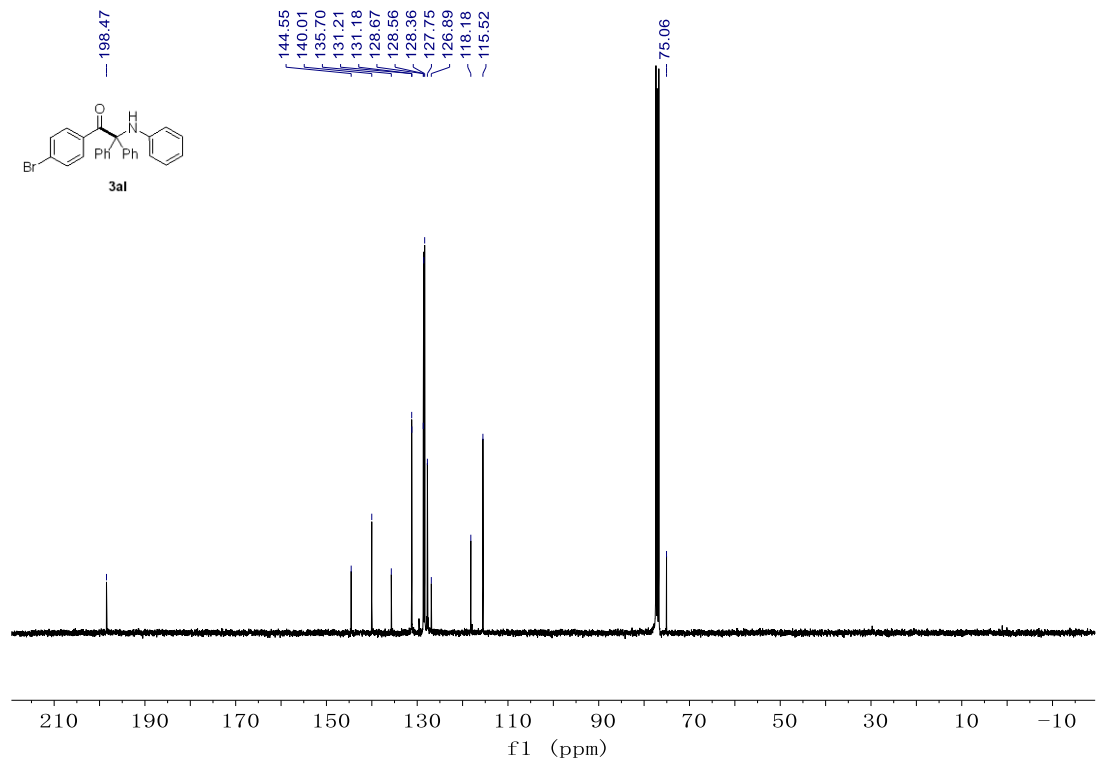
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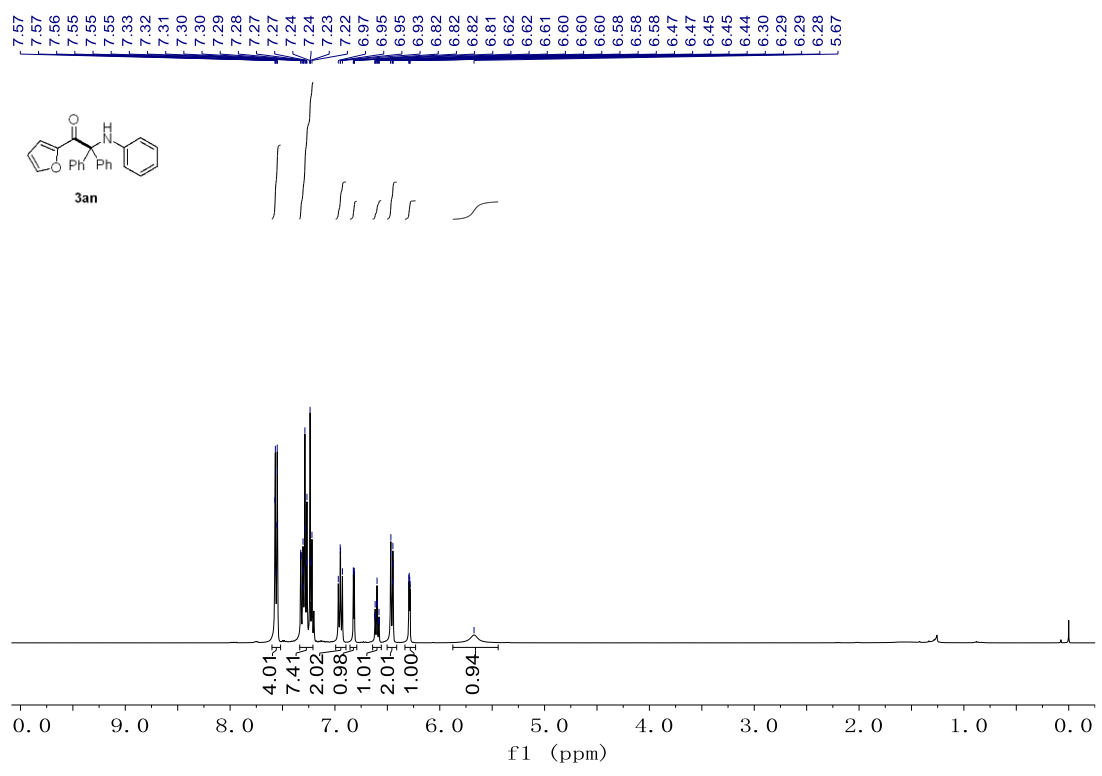
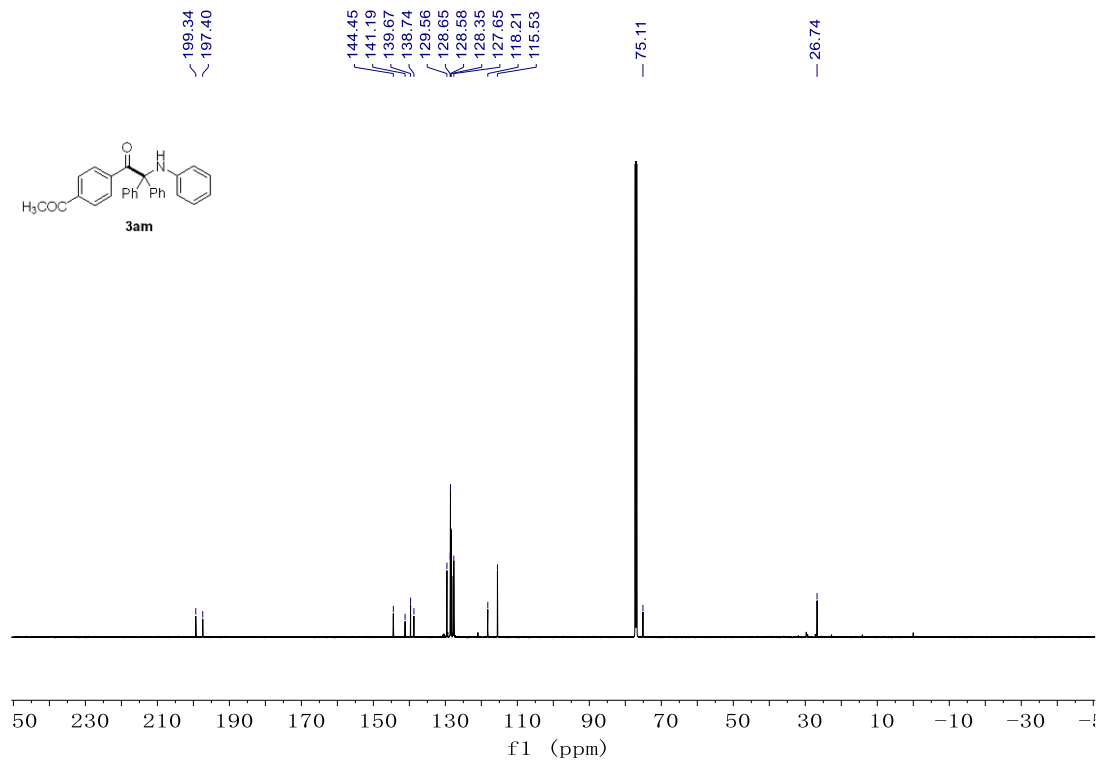


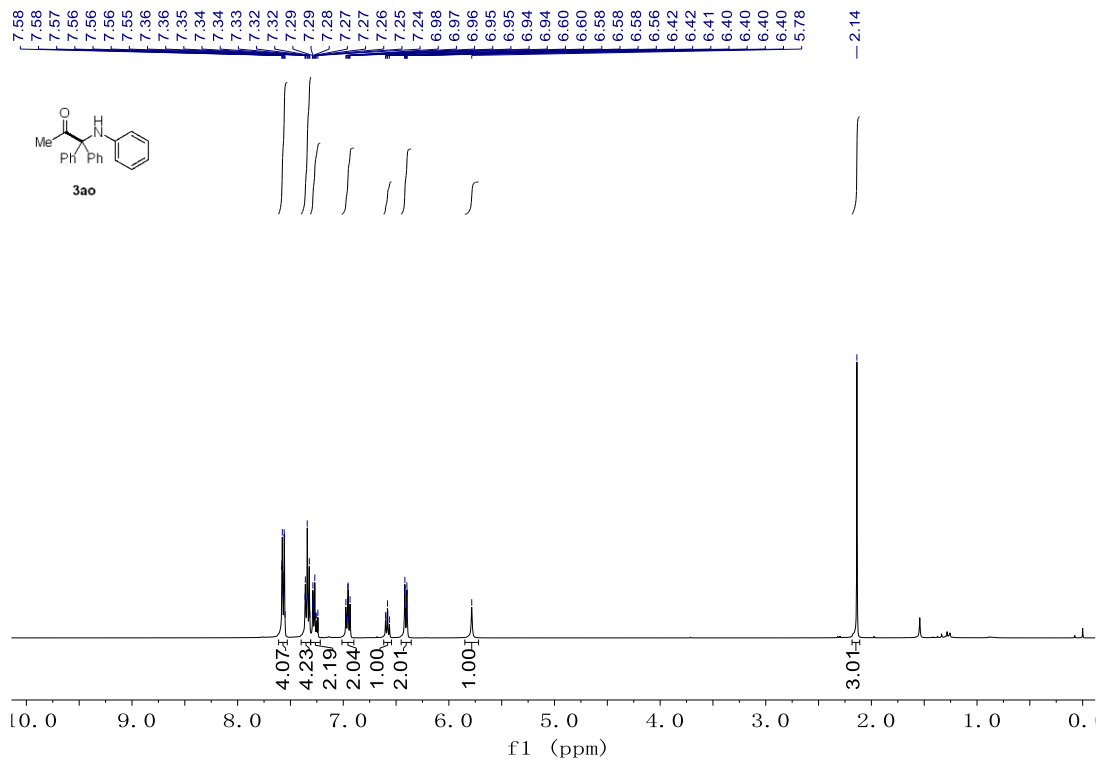
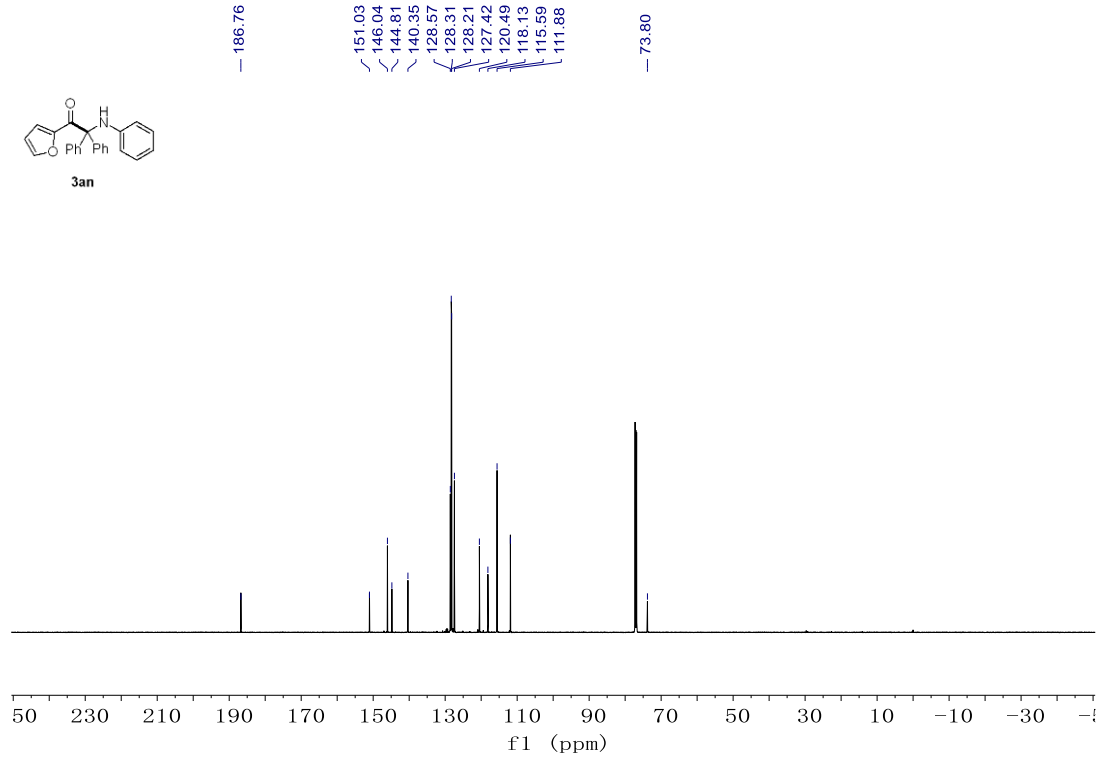
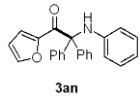


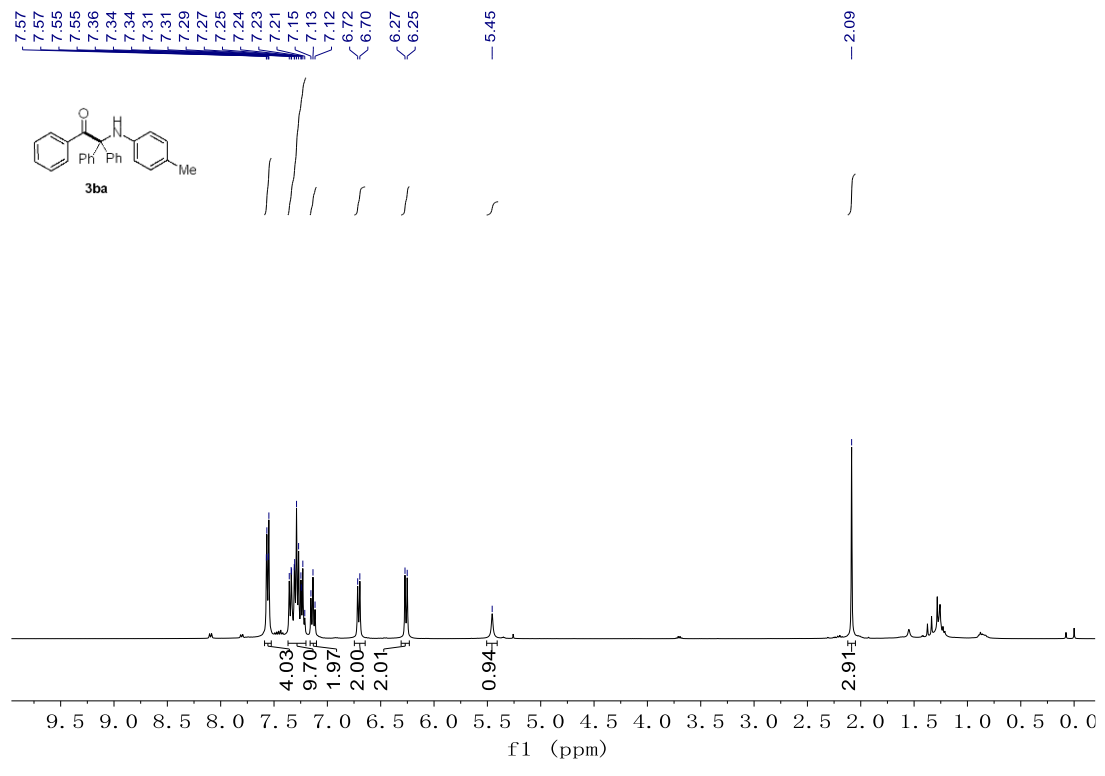
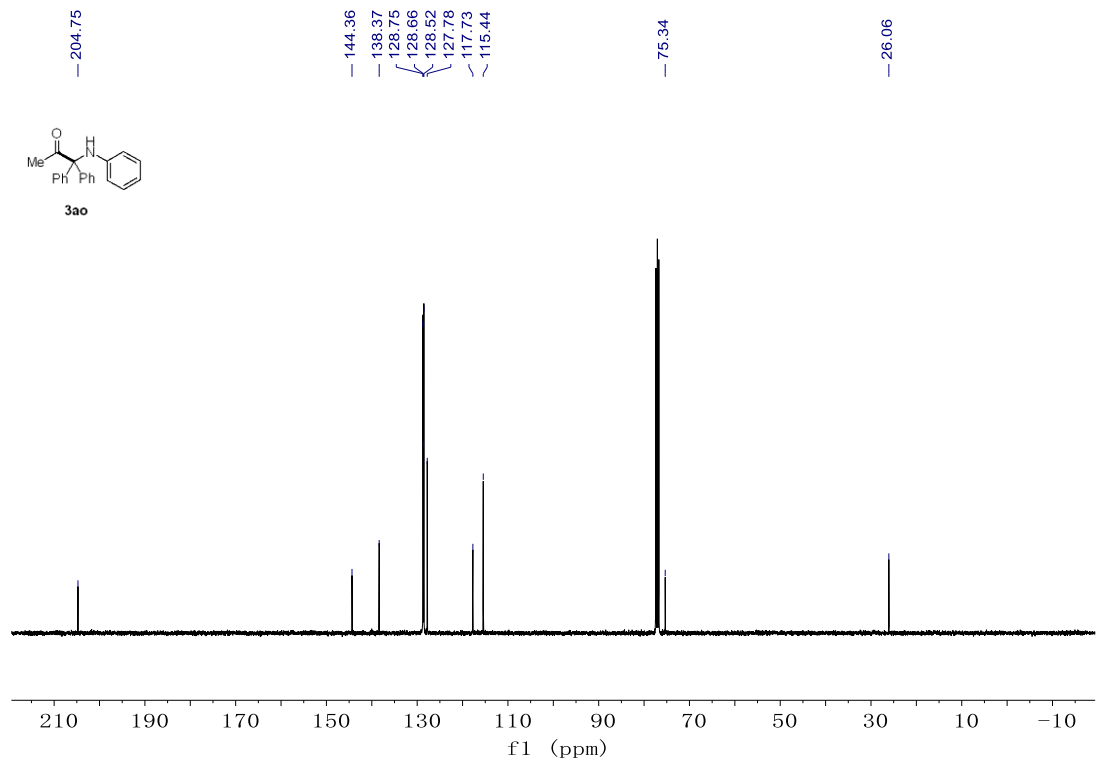


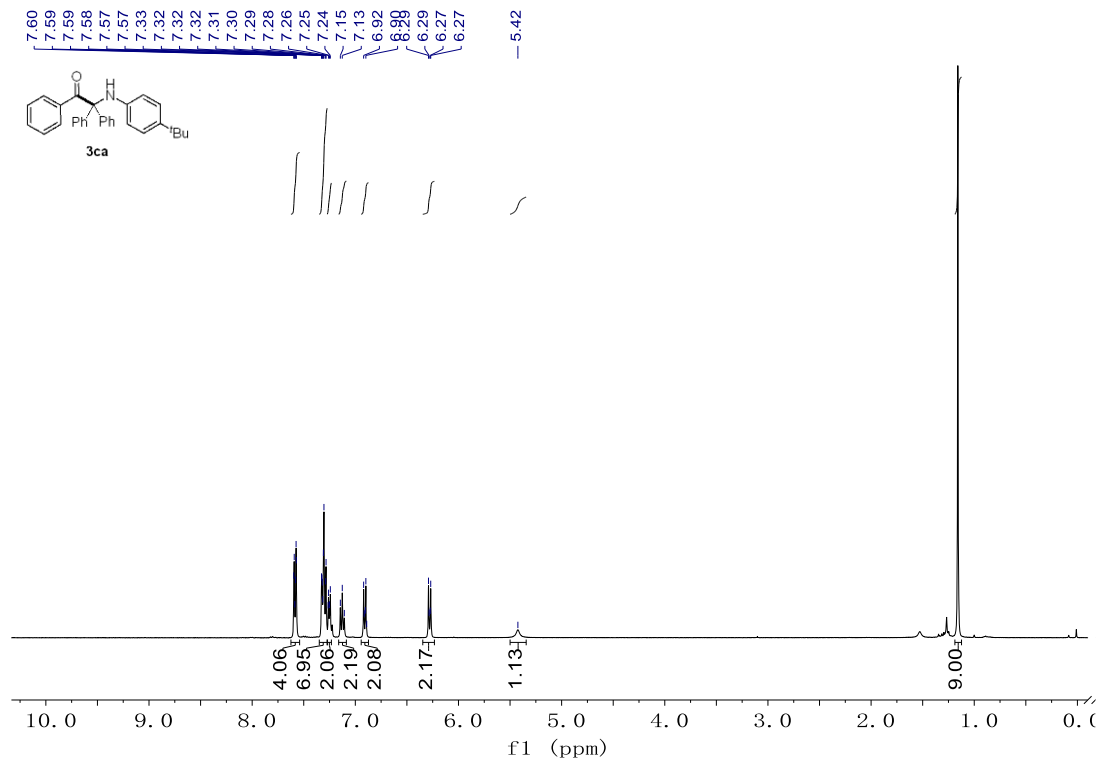
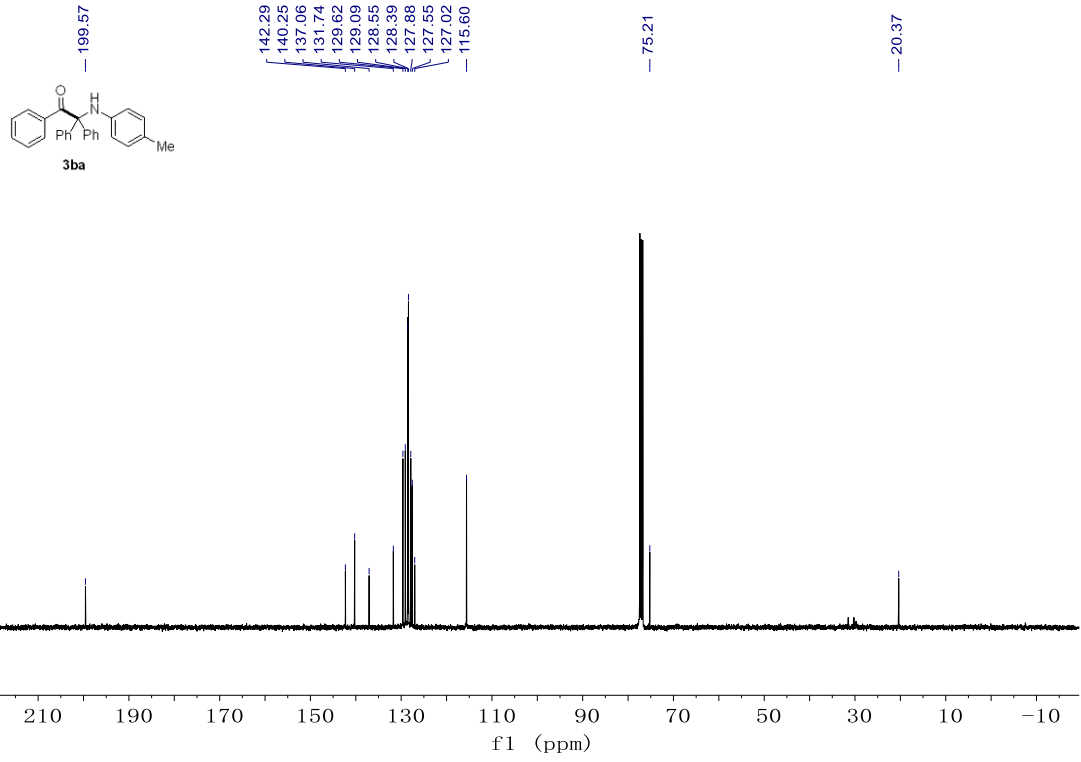


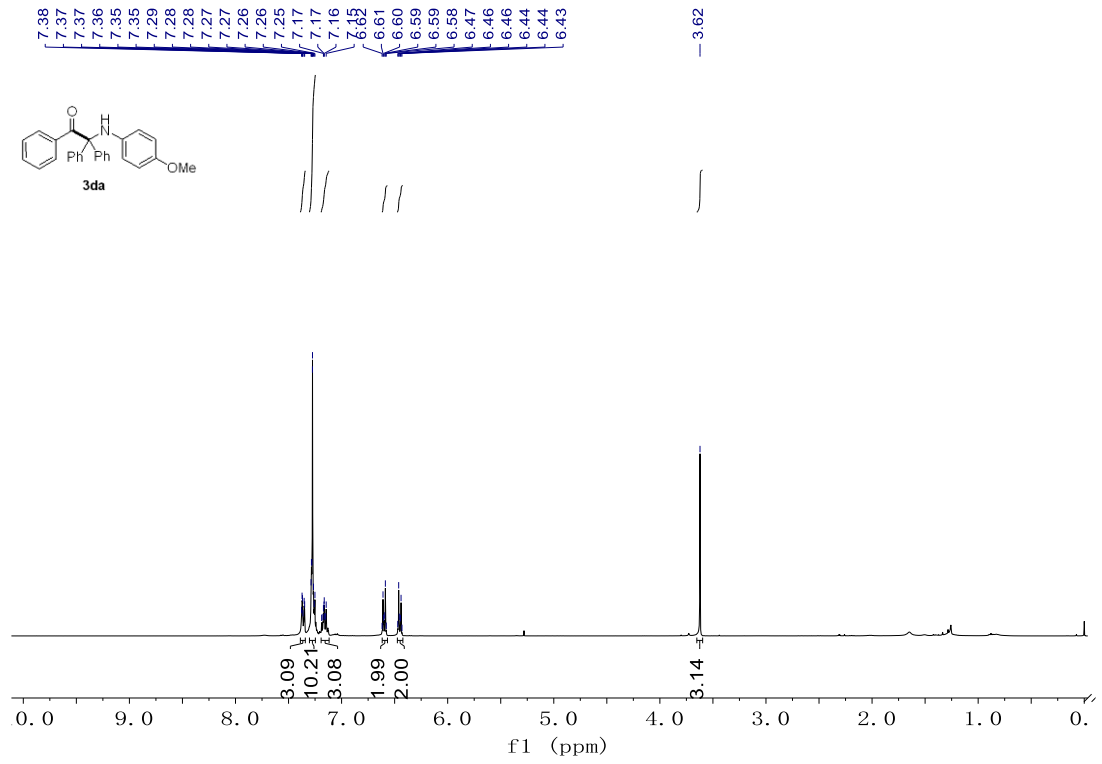
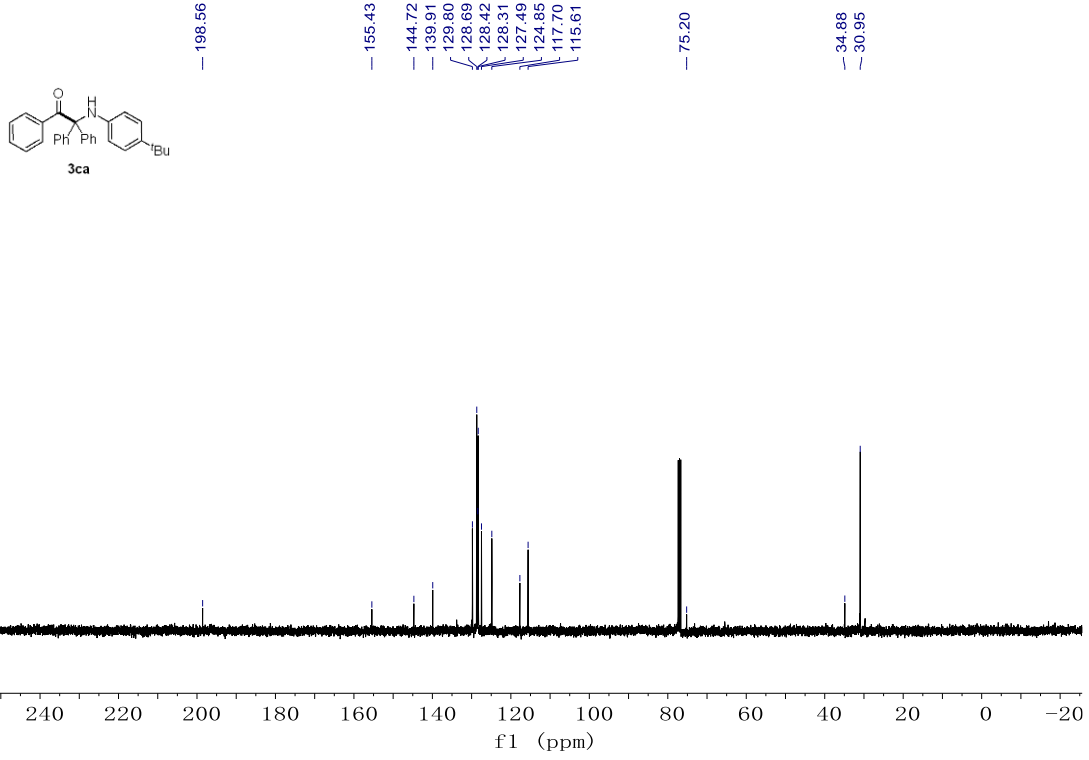


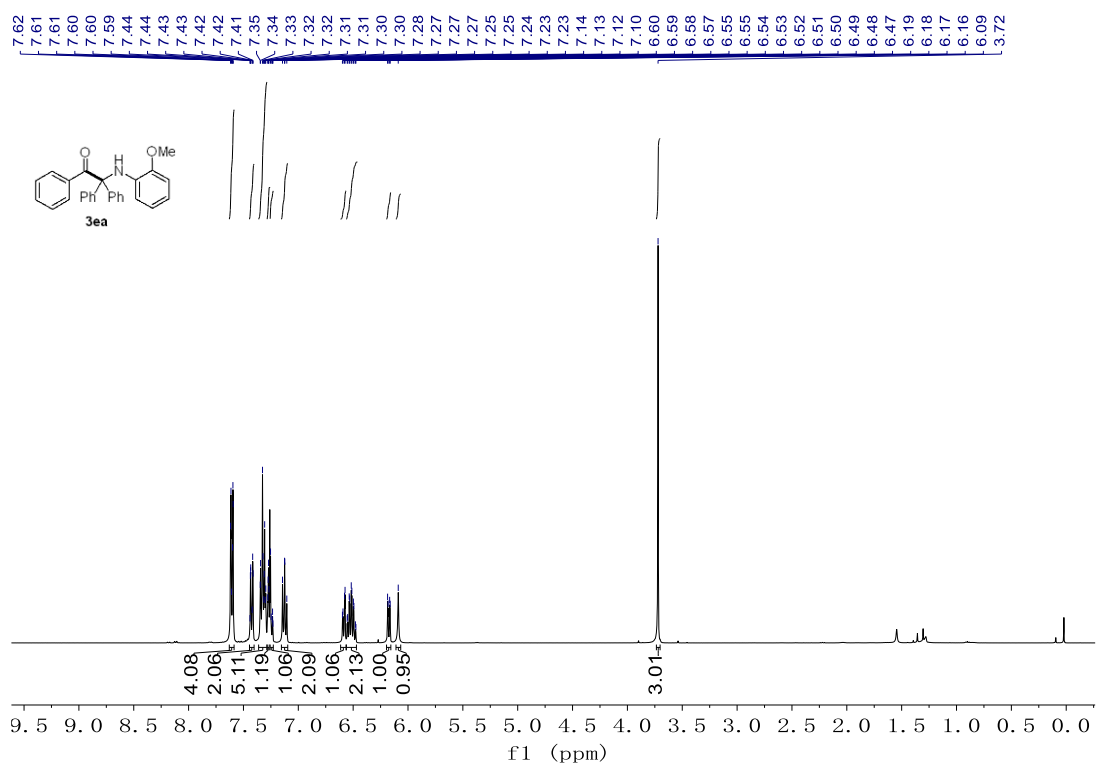
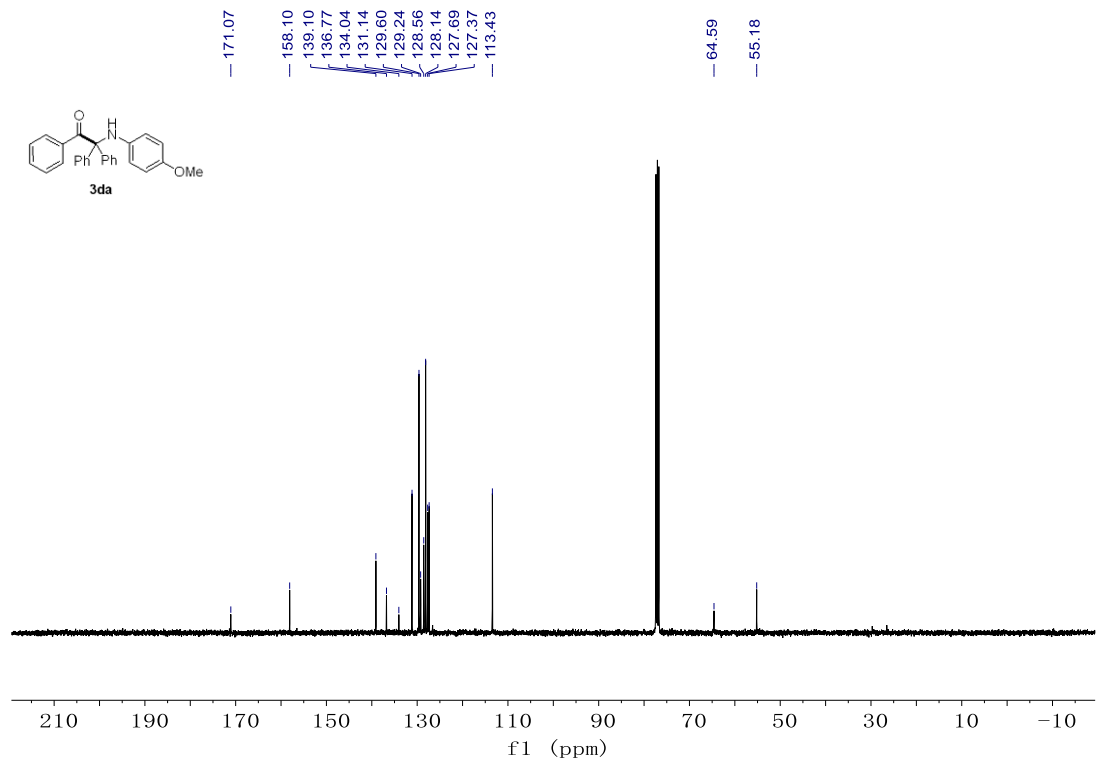


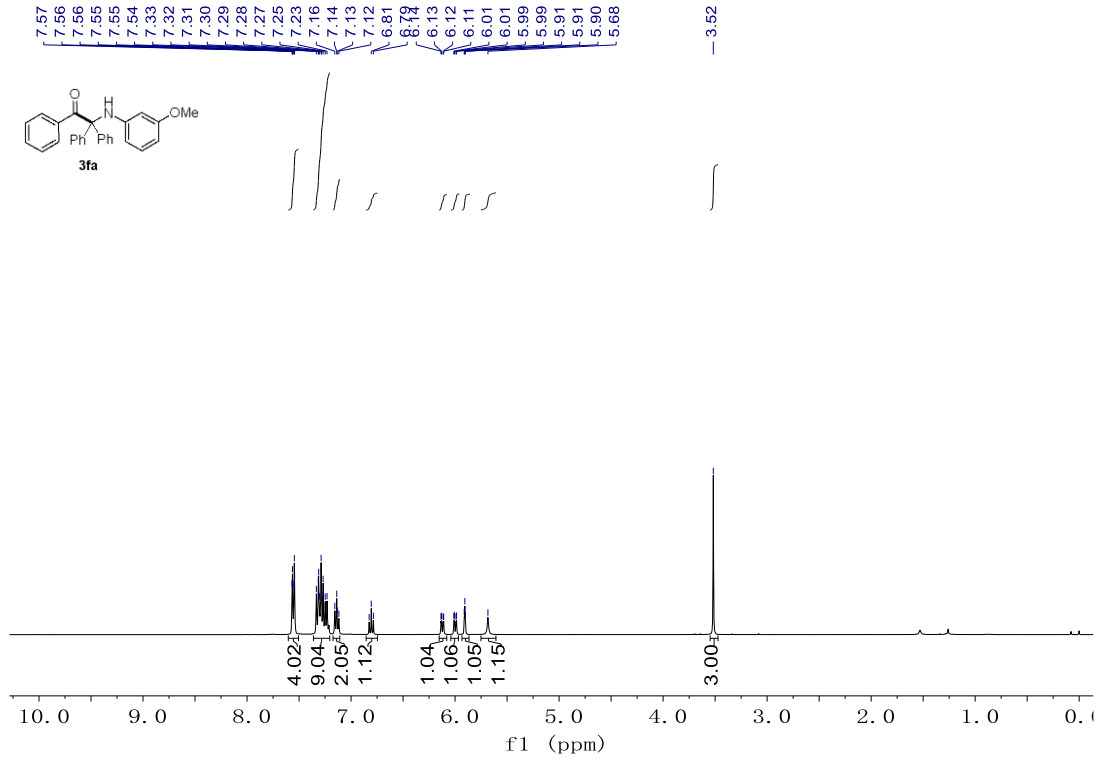
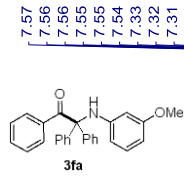
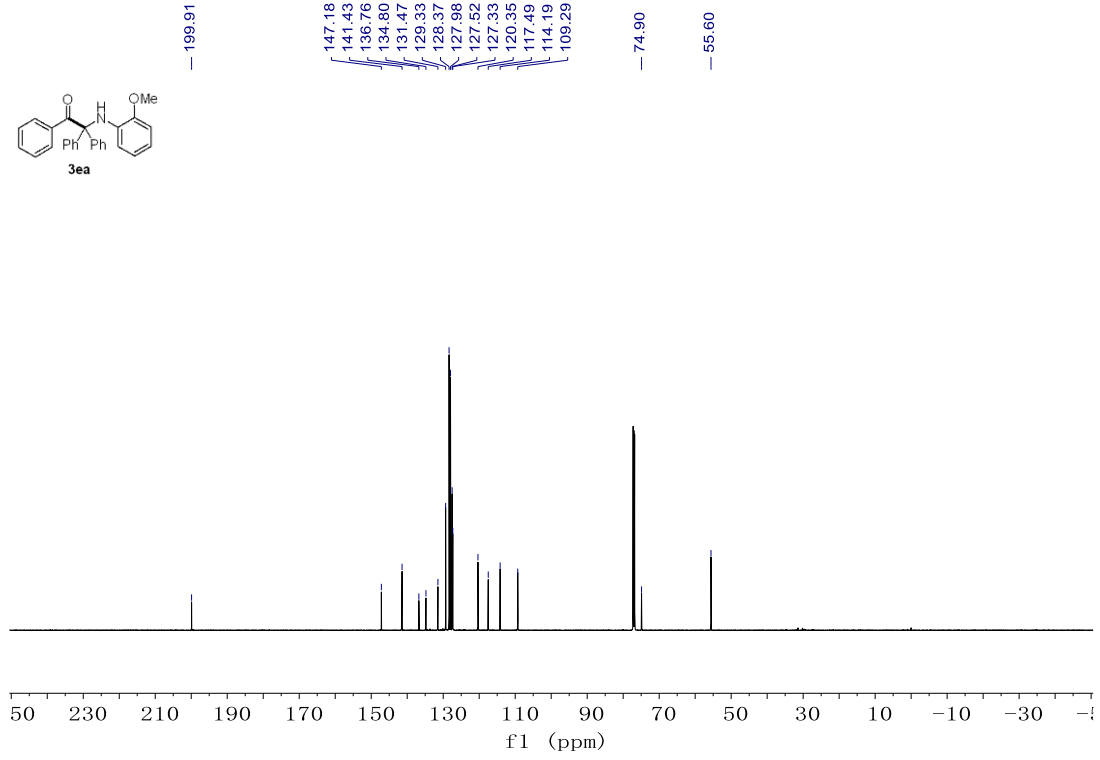
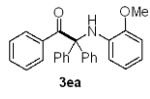


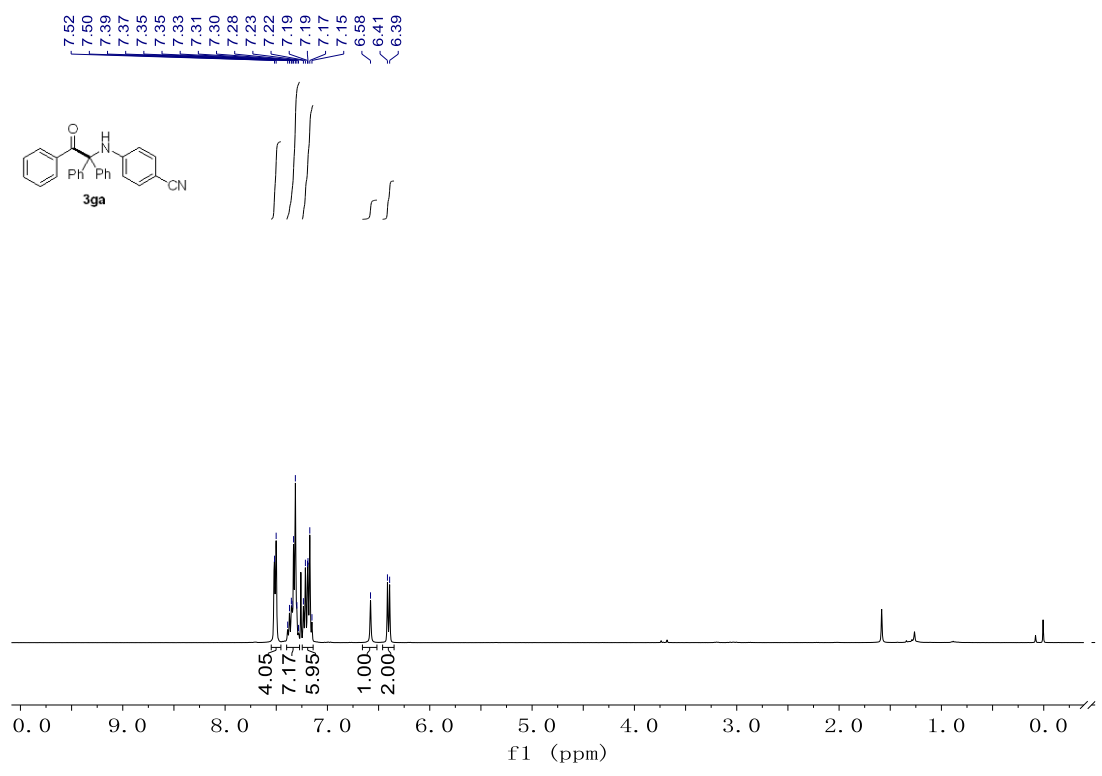
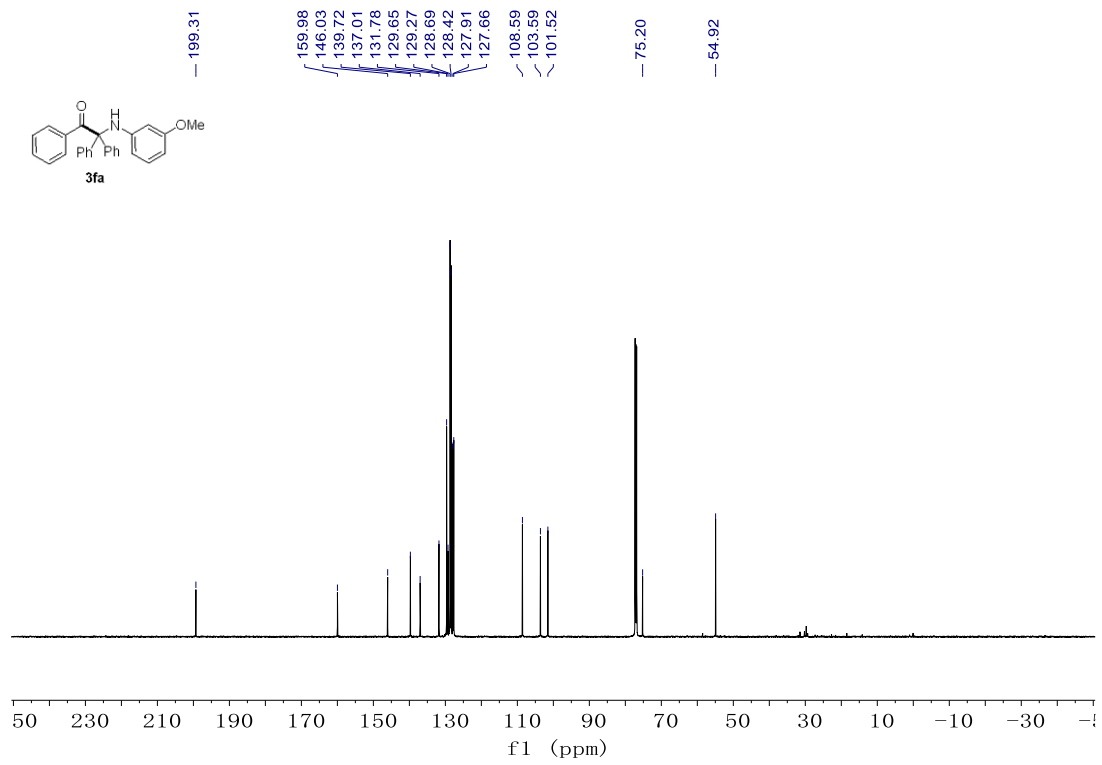


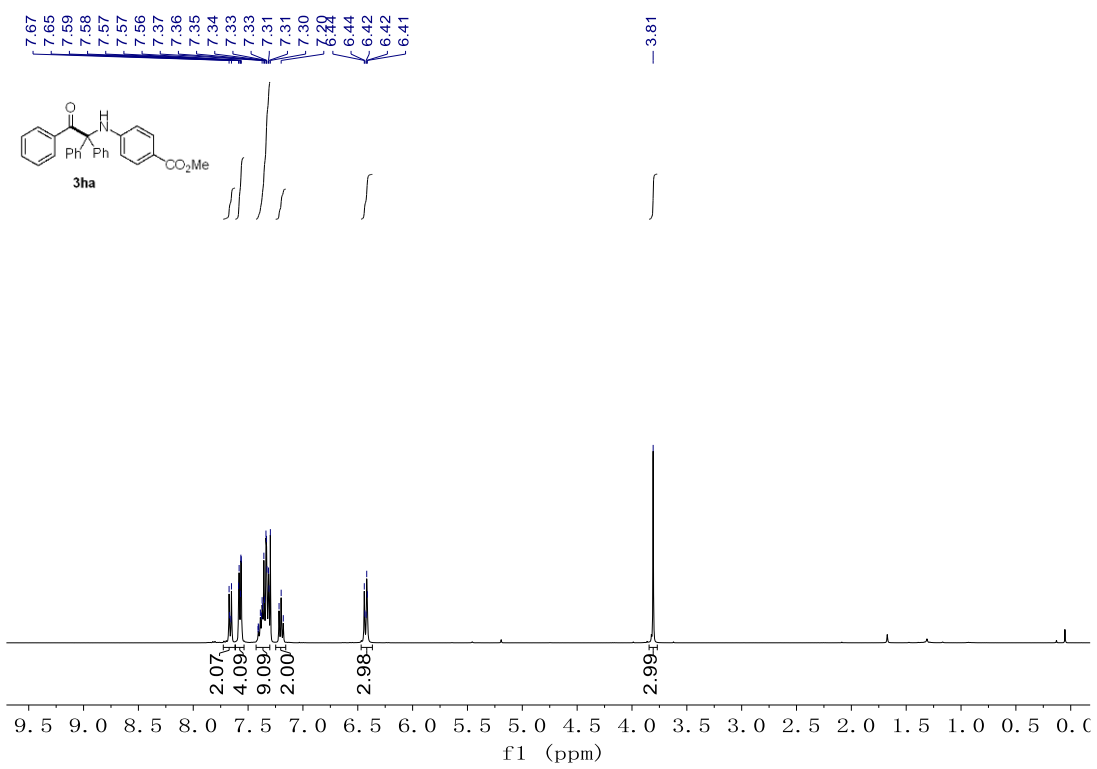
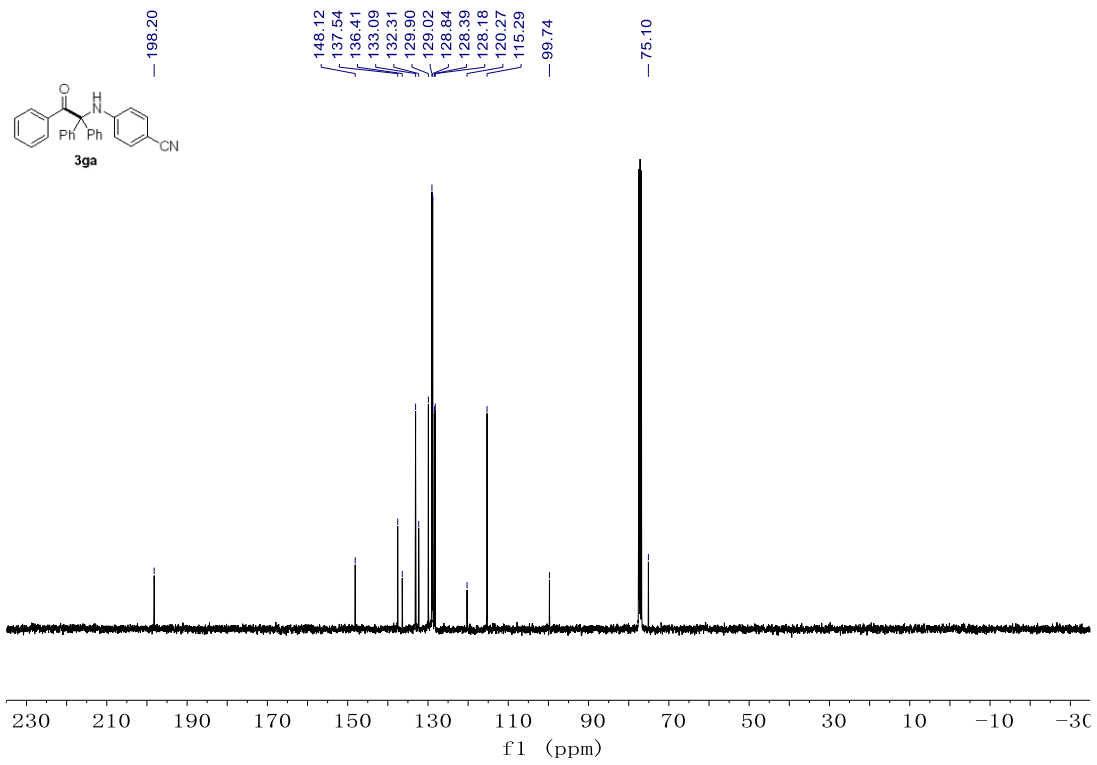


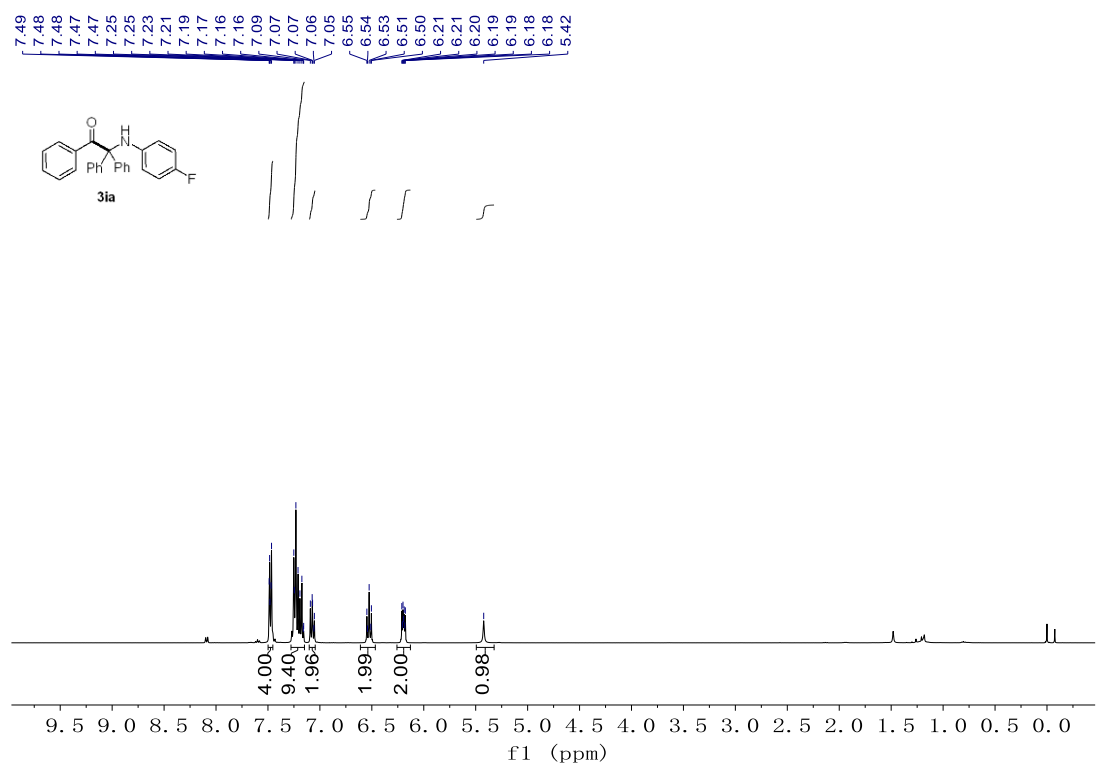
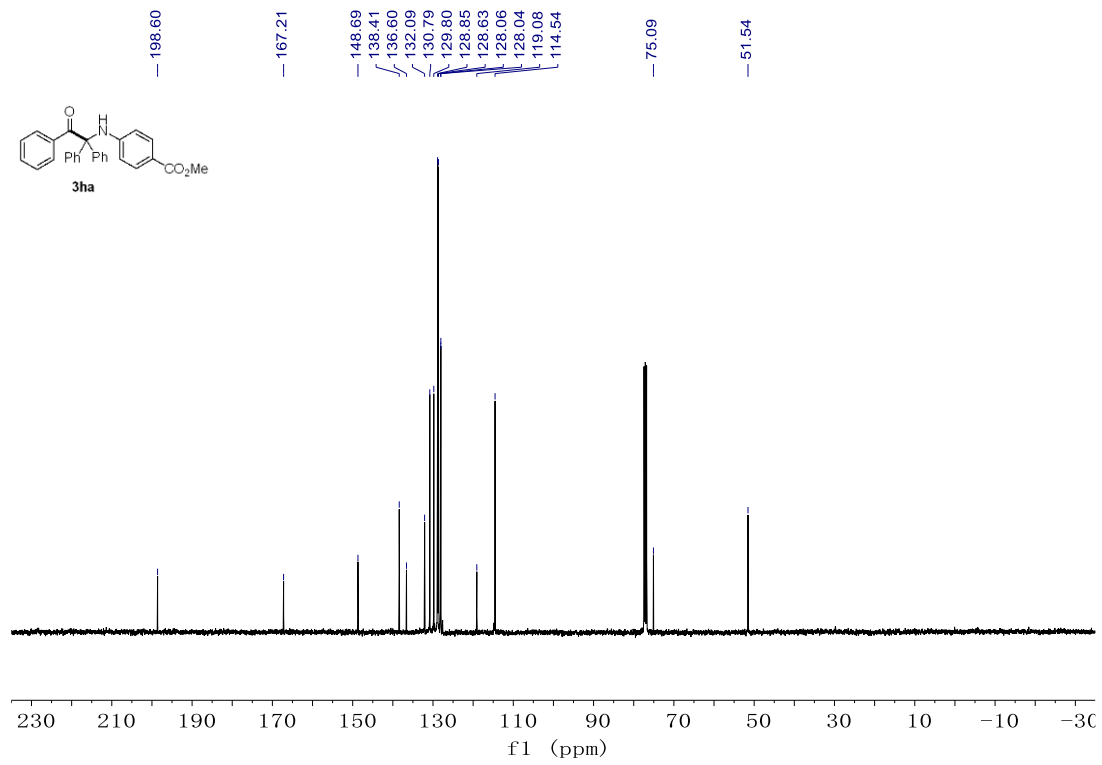


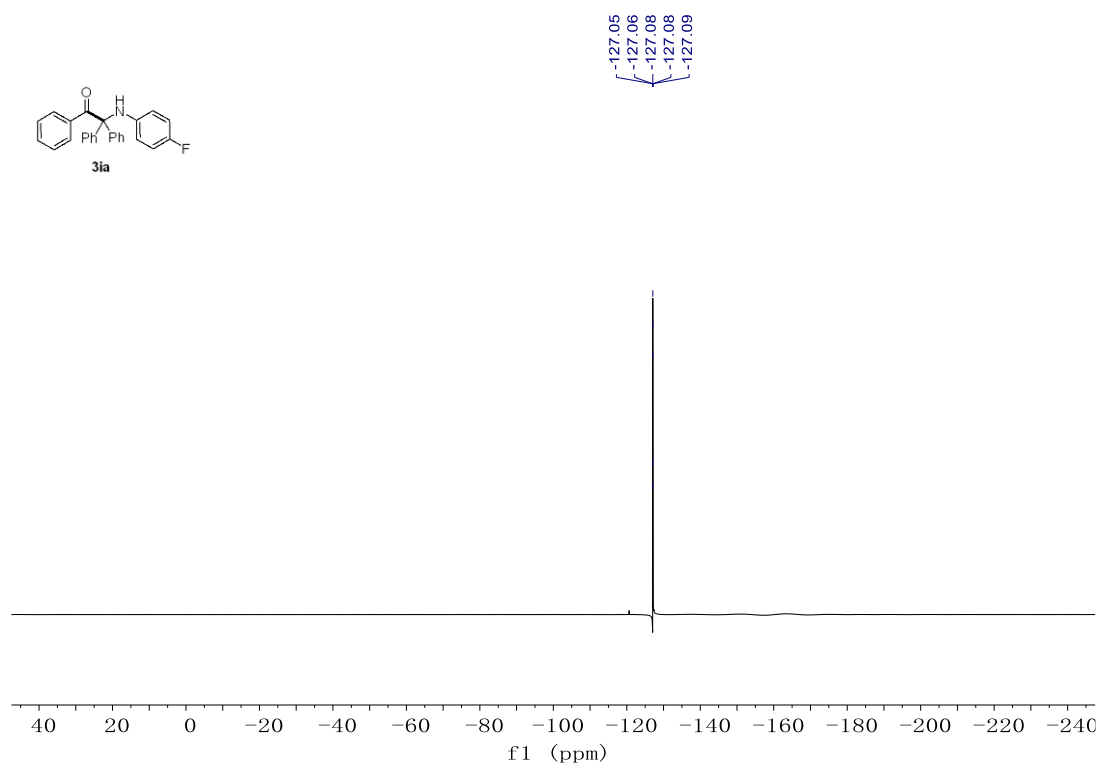
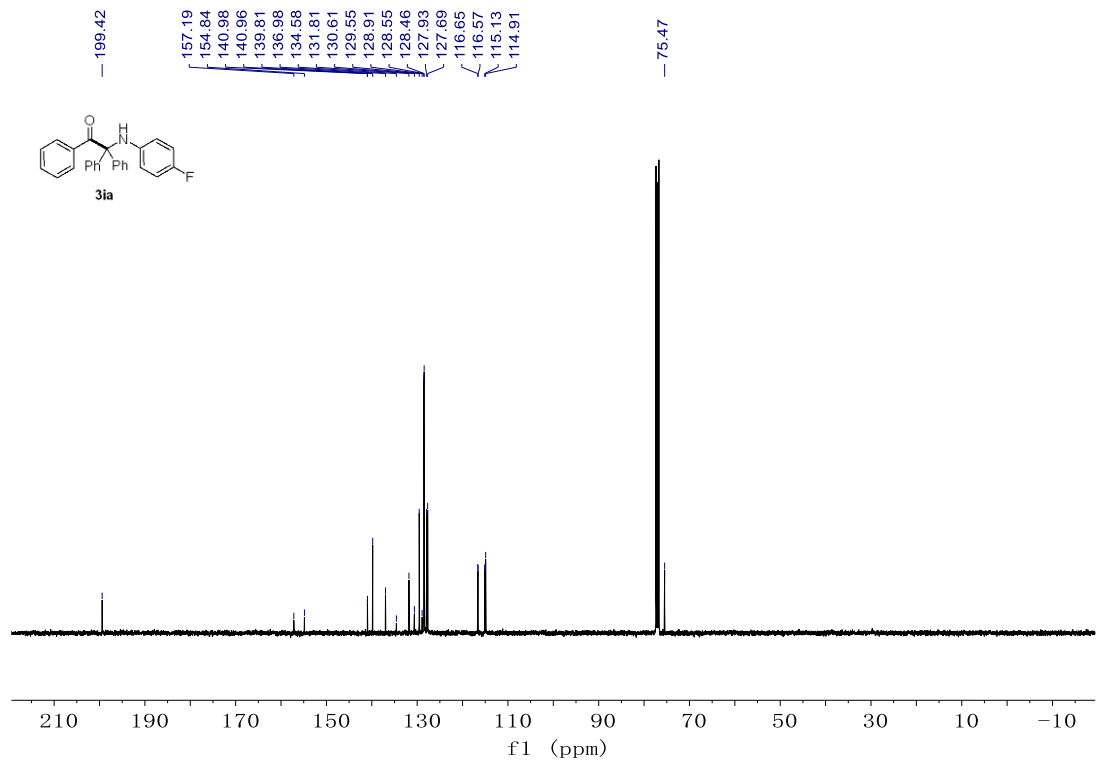


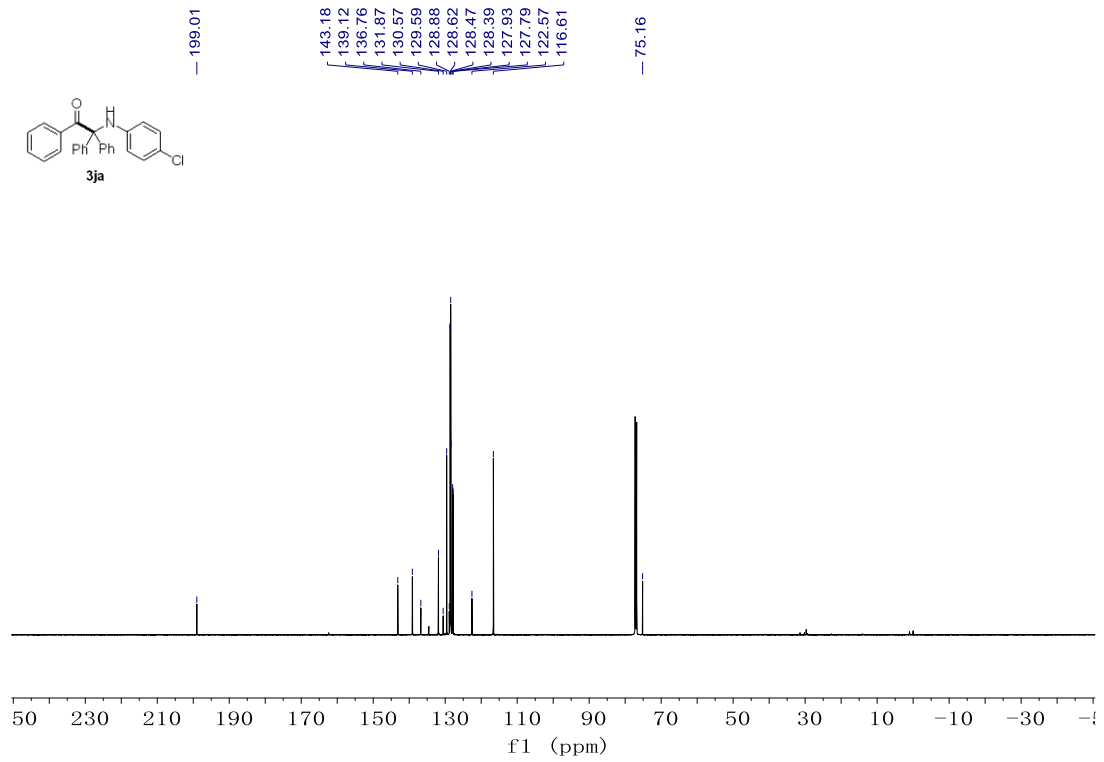
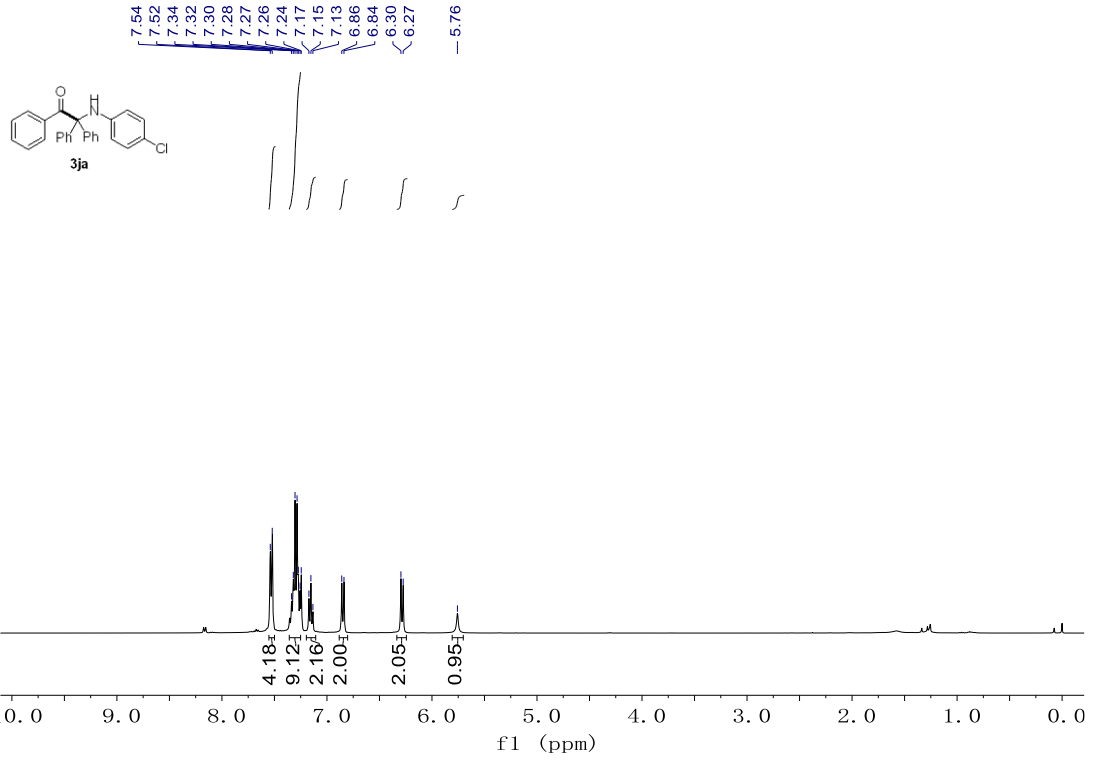


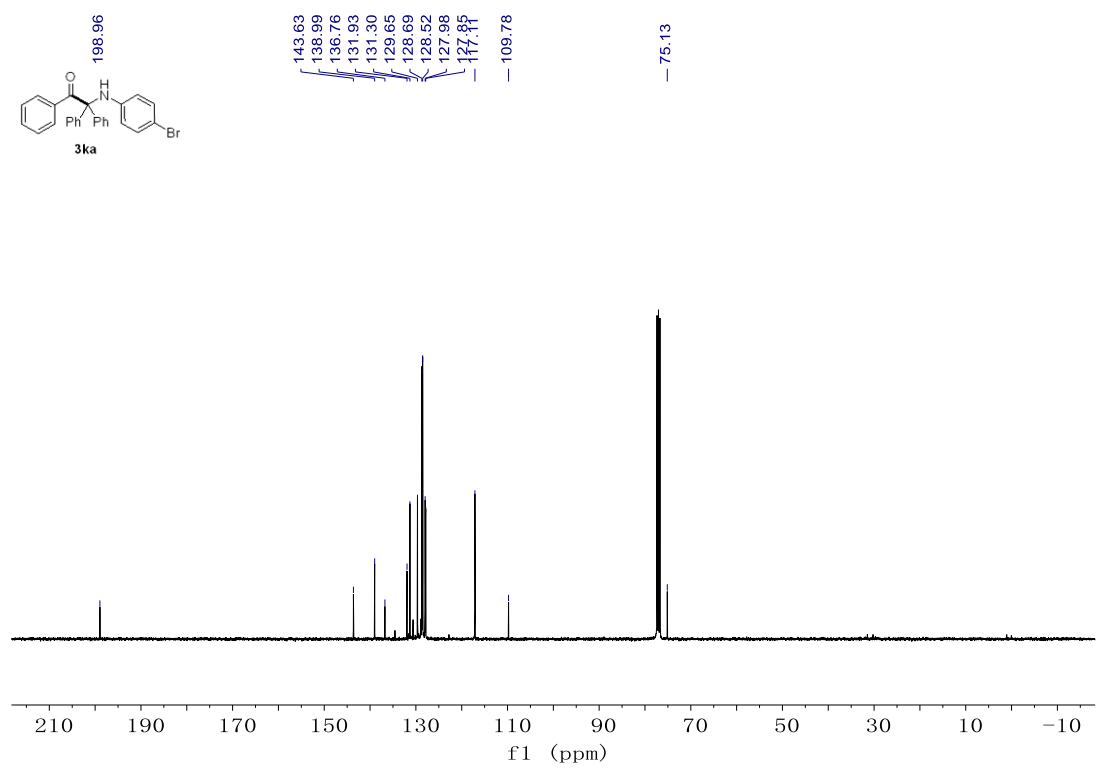
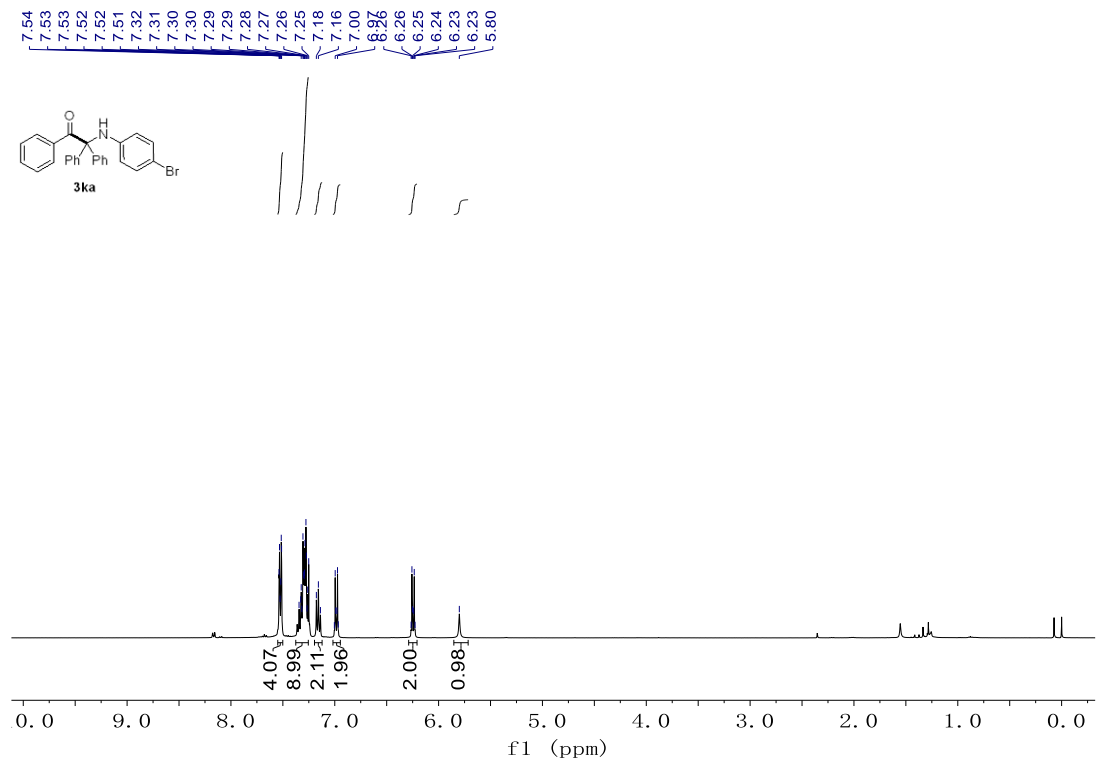


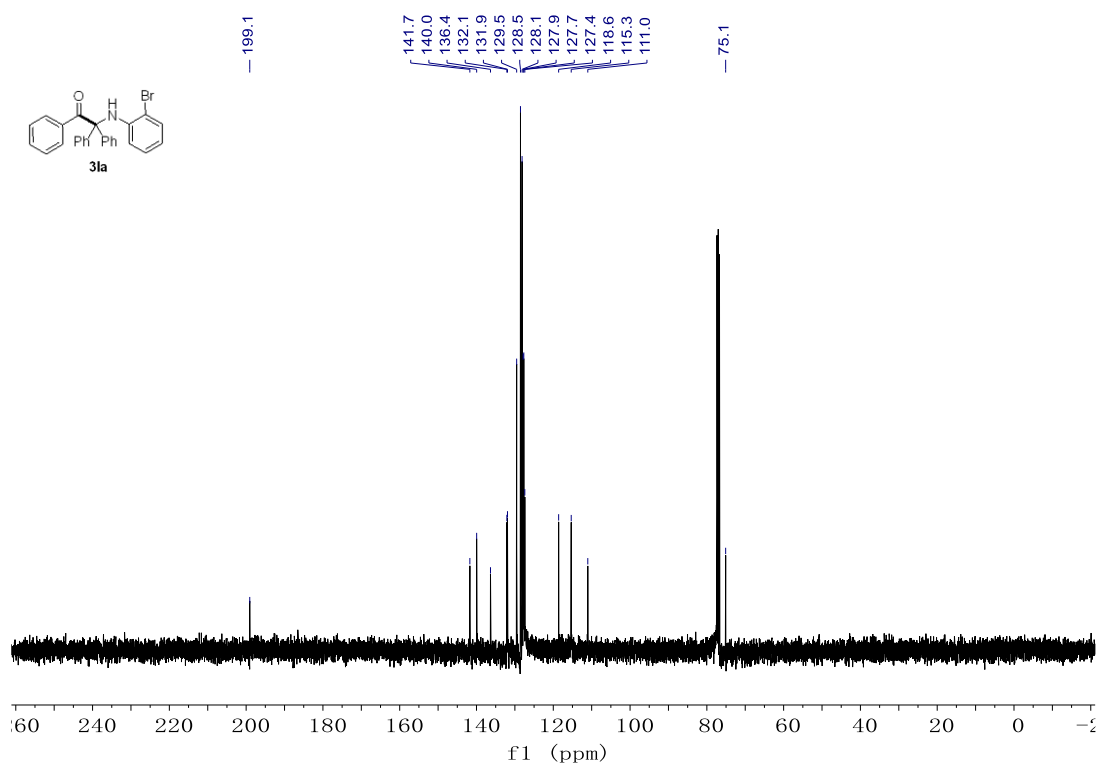
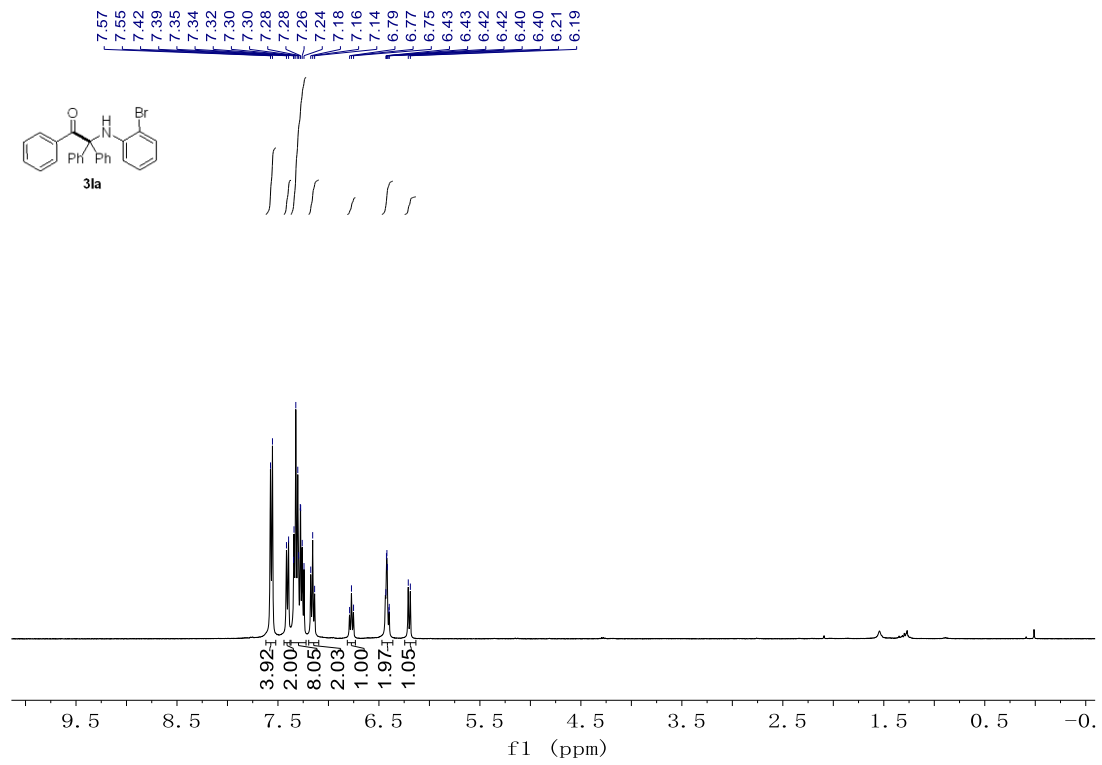




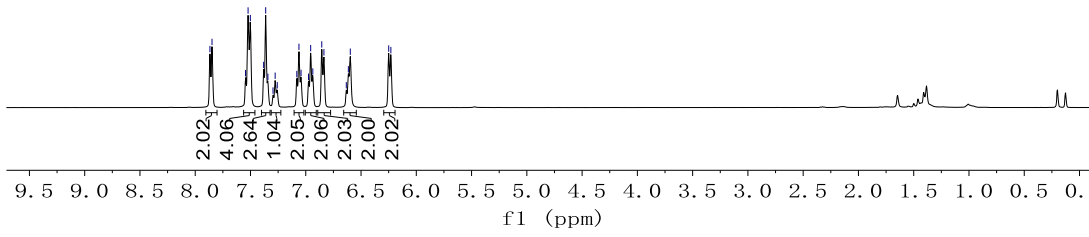
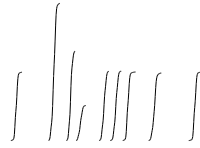
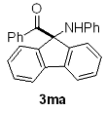




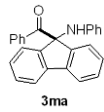




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